# 107 1956

# DOKLADY CHEMISTRY

## PROCEEDINGS of the ACADEMY OF SCIENCES of the USSR

Chemistry Section

ДОКЛАДЫ АКАДЕМИИ НАУК СССР

(DOKLADY AKADEMII NAUK SSSR)

TRANSLATED FROM RUSSIAN

c/b CONSULTANTS BUREAU, NEW YORK

Vol. 107 No's 1-6

March-April 1956

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Section: CHEMISTRY

[redacted]

Vol 107

1956

(A Publication of the Academy of Sciences of the USSR)

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IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU, INC.
227 West 17th Street
New York 11, N. Y.

Qc.773
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Printed in the United States

Annual Subscription $ 95.00

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# BOND ENERGIES AND HETEROGENEOUS CATALYSIS

Academician A. A. Balandin

The majority of reactions of organic catalysis belong to the doublet type: A-B + C-D = A-D + B-C. We consider that they proceed through an intermediate multiplet complex, M. We denote the heat of the first stage, the formation of M, by E' and that of the second stage, the decomposition of M, by E''. Within limits (for details see [1]):

$$E' = (-Q_{AB} + Q_{AK} + Q_{BK}) + (-Q_{CD} + Q_{CK} + Q_{DK}), \quad (1)$$

$$E'' = (Q_{AD} - Q_{AK} - Q_{DK}) + (Q_{BC} - Q_{BK} - Q_{CK}). \quad (2)$$

where Q is the bond energy and K represents the catalyst. The reaction proceeds the more easily (i.e., the specific rate is the greater and the reaction temperature for a given rate is the lower) the less the height of the energy barrier (= E); E is the lesser of the two values E' and E''. Thus, the reaction must proceed more easily the greater is E. The selectivity of the catalyst depends on the chemical natures of the atoms A, B, C, D, K, since Q depends on them. Therefore, a knowledge of bond energies is important in choosing a catalyst.

The present work was provoked by the appearance of compilations of new values of Q (Cottrell [2] and Huggins [3], the latter list being in close agreement with, but less detailed than, the former) and by the necessity for the accumulation of knowledge on catalysis in the field under consideration. In Table 1 is given a list of bond energies important in organic catalysis. The upper part of Table 1 gives the (primarily thermochemical) energies of bonds, $Q_{AB}$, in the molecules (according to [2]). In the last column of Table 1 are entered the energies for the rupture of the first reacting bonds of C = C, C = N, C = O, C = S (for C = O, the average of the values for aldehydes, 81.9 kcal, and ketones, 84.9 kcal., was taken). In the last line of Table 1 is given Q for the reacting atoms with the most studied catalyst, — nickel, $Q_{ANi}$.

TABLE 1

Bond Energies, $Q_{AB}$ and $Q_{ANi}$ in kcal / mole

| | C | N | O | S | H | Cl | Br | F | C= |
|---|---|---|---|---|---|---|---|---|---|
| C | 66.2 | | | | | | | | 46.7 |
| N | 55.5 | 60 | | | | | | | 56.5 |
| O | 77.1 | 44 | 47 | | | | | | 83.4 |
| S | 59 | 115 | (64) | 70 | | | | | 62 |
| H | 90.5 | 84.3 | 110.6 | 87.7 | 104.2 | | | | — |
| Cl | 73 | 37 | 52 | 65 | 103.1 | 57.9 | | | — |
| Br | 60 | 58 | 48 | 56 | 87.4 | 52.1 | 46.1 | | — |
| F | 94 | 56 | 45.3 | 73 | 135 | 60.5 | 50.6 | 37 | — |
| Ni | 6 | 18 | 48.5 | 42 | 55 | 67 | 54 | 98 | $Q_{=CNi}$ = 35 |

The values of $Q_{ANi}$ were determined by us in the following manner. The bond energies of Ni with Cl, Br, F, and S were calculated from recent thermochemical data [4] on the heats of formation of $NiCl_2$, $NiBr_2$, $NiF_2$, and NiS and the data of Table 2. The bond energy of Ni-H was determined in the same way from $NiH_2$ and NiH [4], and was found to be 55 kcal. For the bonds of Ni with C, N, and O, the bond energies, $Q_{ANi}$, were found by comparing the ease with which catalytic reactions proceeded. Such comparisons of fixed values of $Q_{HNi}$, $Q_{ClNi}$, $Q_{BrNi}$, $Q_{FNi}$, $Q_{SNi}$, it appears, fixes the values of $Q_{CNi}$, $Q_{NNi}$, $Q_{ONi}$ with an accuracy of several kilocalories. At the same time, the values of 48.5 for $Q_{ONi}$ found by this method proved to be lower than the thermochemical value of 59 kcal. (from NiO). At present, there are no thermochemical data for $Q_{CNi}$ and $Q_{NNi}$ (we have set up work for their determination), but the values of Table 1 fall in the order C < N < O in agreement with data from inorganic chemistry.

As in all additive systems (as, for example, for molecular refraction), it is necessary to consider constitutive corrections. For doubly bonded C there is introduced the separate value $Q_{=CNi} = 19$ (in the same way as was done for hydrogenation [1,5]). This same value is taken for C in reverse reactions, since $Q_{=CNi}$ refers to the intermediate complex. For example, $Q_{=CNi} = 19$ is used for both hydrogenation and dehydrogenation.

TABLE 2

Heats of Decomposition into Atoms for Elements in Their Standard States [2].

| C | N | O | S | H | K | F | Cl | Br | I |
|---|---|---|---|---|---|---|---|---|---|
| 138 | 85.6 | 59.2 | 66.3 | 52.1 | 21.5 | 18.5 | 28.9 | 26.7 | 25.5 |

For further increasing the precision of the small correction for a double bond, it is probably necessary to introduce also values of doubly bonded N, O, and S. Other constitutive influences are the energy of stabilization or consolidation, $\sigma$, and the influence of substituents at atom A [6], which are partially compensated in catalysis since $Q_{AB}$ and $Q_{AK}$ enter into Equation 1 with opposite signs. Still another correction is the reduction of Q to O° K, which should be done since we are dealing with an elemental process. Certainly, the data of Cottrell must be refined. Thus, for example, $D_{N_2}$, the energy of dissociation of $N_2$, and $\lambda_C$ the sublimation energy of C, must be increased (concerning $D_{N_2}$, cm., see, for example, [7]). However, this does not influence the conclusions [1], since both $Q_{AB}$ and $Q_{AK}$ increase equally in Equation (1). However, according to Steacie [8], $\lambda_C = 141.26$, which is close to $\lambda_C = 138$ kcal. in [2]. Also pertaining to increasing precision is the introduction of individual bond energies. Therefore, Table 1 is still idealized, but is improved in comparison with the corresponding table in [1]. For comparison with the new values of $Q_{ANi}$ earlier values [1] are: $Q_{CNi} = 7$; $Q_{CNi} = 22$ (for hydrogenation); $Q_{NNi} = 16$; $Q_{ONi} = 59$; $Q_{SNi} = 43$; $Q_{HNi} = 53$; $Q_{ClNi} = 66$; $Q_{BrNi} = 50$; $Q_{FNi} = 126$ kcal. For selectivity, it is important only to have the relative values of Q and E, and not their absolute values. Calculations show that the former rules are preserved with the new values of Q. The series for the 20 reactions of Tables 3 and 4 (for substances not containing Cl or Br), which is in agreement with the experiment, was obtained with all 5 values of $Q_{ANi}$ for the number of reacting atoms (H, C, =C, N, O).

TABLE 3

$E_{calc.}$ for Reactions on Ni Catalyst, kcal.

| | C–C<br>H H | N C<br>H N | C–N<br>H H | C–C<br>H O | C C<br>H C | C–C<br>H C | C–O<br>H H | C H<br>N H | C N<br>O H |
|---|---|---|---|---|---|---|---|---|---|
| E' = | −33 | −30 | −28 | −26 | −25 | −25 | −23.5 | −12.5 | −7 |

| | C H<br>C H | C H<br>N H | C H<br>N H | C H<br>O H | C C<br>H Br | H Cl | C H<br>H O | O H<br>H O | N H |
|---|---|---|---|---|---|---|---|---|---|
| E' = | −48.5 | −25.5 | −18 | −17 | 6 | 6 | 14 (E'') | 18.5 (E'') | |

Hydrogenolysis reactions are assembled in the lower series of Table 3. The calculated order of E agrees with that found earlier for known reactions [1], and are confirmed by experiment (over 200 reactions [9]).

The upper series of Table 3 (where C is =C) gives the order of increasing E for the dehydrogenation of hydrocarbons, for the formation of secondary amines from primary (for example, diphenylamine and $NH_3$ from aniline, where the bond C-N approximates = C-N), for the dehyrogenation of amines, for the dehydration of alcohols, for the dimerization of ethylene to butene, for the migration of C = C in the chain, for the dehydration of alcohols, and for hydrogenation of C=N, the first stage in hydramination of ketones. All of the enumerated types of reactions actually proceed over Ni. In the main, this series also agrees with the series in Table 5 of [1]; the chief difference is that hydrogenolysis of the C-C bond now has an E' less than for dehydrogenation (and actually, cyclopentane splits its ring more difficultly than cyclohexane is dehydrogenated). Reactions of sulfur compounds are not in line. They do fall into line if the value for $Q_{SNi}$ is taken as less than the thermochemical value (as for $Q_{ONi}$); however, the reactions of sulfur compounds over Ni have been studied but little. Secondary differences are reactions the relative positions of which are little known. Some values of E in Table 3 were calculated for the first time. For the hydrogenolysis of N-Br and O-Cl bonds [10], calculations by means of Table 1 gives E = E'', -10 and -12, respectively, (or 2 and 5 kcal/mole if solvation of the HCl and HBr formed is taken into account).

TABLE 4

$E^{\prime}_{calc.}$ for Hydrogenation over Ni, kcal.

| | 1 | 2 | 3 | 3a | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| | C=C(H)-C(H) | C=C(H)-O(H) | C=C(F)-H | C(F)=C(H)-H | C=C(H)-O | C(H)-C(H)-O(H) | C(H)-C(H)-C(H) |
| E' = | −3 | −10 | −11 | −12 | −16 | −17 | −48.5 |

In Table 4 are given values of E' for reactions which can occur during the hydrogenation of furan compounds over Ni; E' was calculated by means of Equation (1) and Table 1.

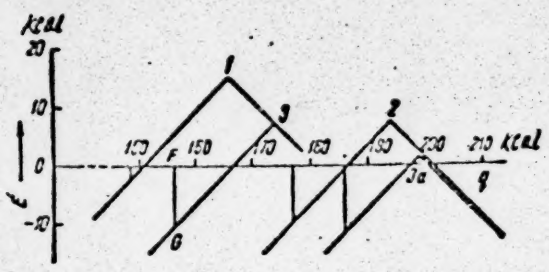


Fig. 1.

Peak 3 of the volcano-shaped curve for the hydrogenation of the furan C=C bond (see Figure 1) lies significantly below (by 8 kcal) peak 1 of the curve for the hydrogenation of the olefinic C=C due to the presence of stabilization energy ( $\sigma$ = 16) [11] and to the fact that the ordinates of the peaks are equal to half the heats of reaction, Q. It is natural that |E'| – the distance lengthwise to the ordinate axis – is greater for Reaction 3 than for Reaction 1 [but less than for the hydrogenation of the C=O bond (Curve 2)]. For purposes of calculation, we assumed that M still contains (as a maximum) half of $\sigma$. Then, the heat of formation of the intermediate complex in the hydrogenation of the furan bond is

$$E^{\prime}_{f} = (-Q_{C=C(F)} - \sigma) + 2Q_{CFNi} + {}^{1}/_{2}\,\sigma + (-164.2 + 2Q_{HNi}). \qquad (3)$$

Comparing Equation (3) with Equation (1) for the hydrogenation of olefinic bonds (where we denote E' by $E^{\prime}_{e}$), we see that $E^{\prime}_{f} = E^{\prime}_{e} - \sigma/2$ and $Q_{C(F)Ni} = Q_{=CNi} + 4$. Other reactions where $\sigma$ takes part may be treated analogously. Thus, in view of the deformed nature of M, it is possible to obtain E' for Reaction 3 by subtraction of 8 kcal from E' for Reaction 1, and E' for the hydrogenolysis of the ether bond of furan can be obtained by subtraction of 8 kcal. From E' for the hydrogenolysis of =C–O bonds. These values have been included in Table 4. Table 4 shows that during the hydrogenation of derivatives of furan an olefinic bond in a chain is hydrogenated easiest of all, then (in order of increasing difficulty): a carbonyl bond in a chain, the C=C(F) in the furan ring, then comes the formation of spirane, the rupture of C-O in a chain, and – at the very highest temperature – rupture of the C-C bond. Decomposition of the ether bond in the furan ring, C-O(F) (E' = −12)(Curve 3a, Figure 1), during hydrogenation over Ni almost does not proceed, since the C=C(F) bond (E' = −12) is hydrogenated first, whereupon the furan system disappears, and hydrogenolysis of the ordinary C-O bond proceeds with difficulty (E' = −17 kcal). It has recently been found [12] that the ether bond is partially affected, but at higher temperatures in agreement with Table 4. The order given in Table 4 is confirmed by more than 80 transformations of furan derivatives [5].

The profile of the potential energy of the dehydrogenation alcohols over Ni, presented previously [13], appears somewhat changed when using the figures of Table 1 [see Figure 2 (for a primary alcohol)].

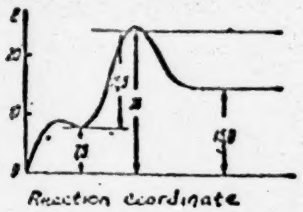


Fig. 2.

Reactions involving shortening of the carbon chain by the action of $CO_2$ [14] over Ni (as well as related reactions) are explained, as before, by the fact that the values of E for the different stages in [14] differ from those calculated from Table 1 by several kilocalories. Also in conformity with Table 1 is the reduction of halogen derivatives by hydrogen over carbon [15] which is impeded, not by the adsorption of the starting material, but by the desorption of HCl and HBr; E' > 0, E'' < 0.

In previous work [16-18], $Q_{AK}$ has been investigated wih various catalysts, the values being determined,

not by thermochemical, but by the catalytic method – from the dehydrogenation of hydrocarbons (I), from the dehydrogenation of alcohols (II), and from the dehydration of alcohols (III). Substitution for the system of bond energies $Q_{AB}$ from [1] of the system from [2] leads to only small corrections: 1.5 kcal. should be subtracted from $Q_{HK}$ given in [16-18], 5.0 kcal. should be added to $Q_{CK}$ and 2.1 kcal. should be added to $Q_{OK}$. After making such corrections for Reactions I, II, and III, the half sums of the energies of breaking and making bonds will be $s/2$ = 165.4; 194.3; 162.5; and $u/2$ = −13.4; −6.7; −5.1; instead of the former $s/2$ = 159; 190; 154; and $u/2$ = −13.0; −7.5; and −3 kcal., respectively. This merely shifts the volcano-shaped curves somewhat. The bond energies $Q_{AK}$, determined by kinetics for chromium oxide are: $Q_{HCr}$ = 54.7; $Q_{=CCr}$ = 11.0; $Q_{OCr}$ = 71.8 kcal., and, at present, appear to be fairly close to the data of Table 1 for Ni.

The adsorption potential, q, for $Cr_2O_3$ from [19] is changed by only +4 for $q_{H_2}$ and + 11 for $q_{H_2O}$, while from the change of origin $q_{H_2}$ is changed from 169 to 189 and $q_{H_2O}$ from 117.5 to 142 kcal. The coordinates of the volcano-shaped curves are similar to those stated above.

Thus, changing from the former system of bond energies [1] to the new improved one (Table 1) does not change the earlier conclusions. The selectivity of catalytic action can be expressed through bond energies with the catalyst, $Q_{AK}$. It is new that in some cases $Q_{AK}$ appears to be somewhat lower than the thermochemical values; this is an interesting principle.

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Received September 24, 1955



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* T.p. = C.B. Translation pagination.

# THERMAL CHLORINATION OF PROPANE

B. A. Krentsel, Academician A. V. Topchiev and D. E. Illyina

The question of the chlorination of propane has been discussed comparatively little in the literature, there being only a few works by foreign investigators[1-3]. Meanwhile, the preparation of chloro derivatives of propane assumes considerable interest both from the point of view of broadening our ideas on the mechanism of chlorination reactions of the lower paraffinic hydrocarbons and in connection with the use of chloropropanes of various degrees of substitution in industry.

## EXPERIMENTAL

The chlorination of propane was carried out in a laboratory flow-type apparatus. Propane from a cylinder passed successively through scrubbers filled with 98% sulfuric acid and 20% solution of sodium hydroxide, respectively; then through a drying column filled with calcined calcium chloride. The amount of propane was measured with a rheometer following the drier. Chlorine was passed from a cylinder through a scrubber filled with 98% sulfuric acid; a rheometer, and entered a mixing vessel where it was mixed with propane in the desired proportion. From the mixing vessel, the mixture of reacting gases passed into the reaction tube, which was located in an electric furnace fitted with a temperature controller. The temperature in the reaction zone was measured with a thermocouple and galvanometer. The reaction products from the reaction tube were passed into a receiver fitted with a reflux condenser and then into a system of traps cooled successively by ice and a freezing mixture of solid carbon dioxide and isopropyl alcohol. The unreacted propane and the hydrogen chloride formed in the reaction were passed to a spray-type water scrubber for recovery of the hydrogen chloride.

In separate experiments, the quantity of unreacted chlorine was determined by means of a solution of potassium iodide (titration of the liberated iodine with hyposulfite). The liquid reaction products were washed with water, neutralized with a 20% solution of soda, and then, after a second water wash, were dried over calcined calcium chloride. The composition of the original propane as determined by low-temperature fractional analysis was: $C_3H_8$, 95.3 weight %; $C_2H_6$, 4.2 weight %; $C_4H_{10}$, 0.5 weight %.

The dependence of the degree of chlorine consumption on the temperature in the reaction zone. With the aim of determining the temperature limits for the thermal chlorination of propane, a study was carried out on the dependence of the degree of chlorine consumption on temperature. The experiments were carried out with a mole ratio of $C_3H_8 : Cl_2$ of 2 : 1 and at a space rate of 30 hours$^{-1}$. The data thus obtained are presented in Table 1 and Figure 1 (Curve 1), from which it is seen that, during the thermal chlorination of propane a chlorine consumption of 100% was reached at a temperature of 300°.

TABLE 1

| Temp., °C | 175 | 202 | 220 | 223 | 227 | 241 | 244 | 263 | 298 | 300 |
|---|---|---|---|---|---|---|---|---|---|---|
| Reacted chlorine, % | 5.8 | 7.9 | 27.9 | 29.8 | 40.2 | 69.4 | 77.5 | 98.2 | 99.2 | 100.0 |

It was shown by us previously [4] that filling the reaction zone with an inert packing, for example, with pieces of glass rod, had a substantial influence on the degree of chlorine consumption at comparatively low reaction temperatures during the thermal chlorination of n-butane. In this connection, it was interesting to investigate, in this case, the influence of an inert surface on the chlorination of propane. For this purpose, in a separate series of experiments the reaction tube was filled with pieces of glass rod (total surface, 380 cm$^2$).

As may be seen from Figure 1 (Curve 2), in this case the chlorination of propane began at a lower temperature, and, within comparable temperature limits, chlorine consumption in the empty tube was lower than in the packed tube. This is especially noticeable at temperatures up to 230-240°. However, as we observed during the

chlorination of n-butane, complete chlorine consumption in the empty tube and in the tube filled with inert packing was reached at a temperature of 300°.

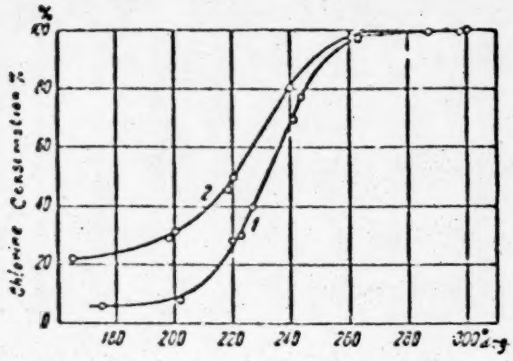


Fig. 1. Dependence of the degree of chlorine consumption on temperature. 1) Empty tube; 2) packed tube.

From the point of view of a chain reaction, the results can be explained in the following manner. At low temperatures, at which chlorination began in the packed tube, the rate of chain formation on the surface predominated over the rate of chain breaking on the surface. At these temperatures, consequently, an increase in surface-to-volume ratio necessarily led to facilitation of the reaction, as was observed in our experiments (the lower temperature of reaction initiation and the greater degree of chlorine consumption in the packed tube in comparison with the empty one). With an increase in temperature, the rate of chain breaking on the surface approached (or surpassed) the rate of their formation on the surface. The possibility that, with an increase in temperature, the emergence of homogeneous chain formation began to have an effect is not excluded. The increase in temperature could not have had an effect on chain breaking in the open space, which in the given reaction, must have been the result of three-body collisions.

TABLE 2

Dependence of the Yield of Chlorination Products on Space Rate.

| Experiment No. | Temp., °C | Experiment duration, min. | Mole ratio $C_3H_8 : Cl_2$ | Space rate, hour$^{-1}$ | Product composition, weight % | | |
|---|---|---|---|---|---|---|---|
| | | | | | Monochloropropanes | Dichloropropanes | Trichloropropanes |
| 93 | 310 | 265 | 0.94 : 1 | 46 | 48.2 | 41.0 | 10.8 |
| 99 | 315 | 220 | 0.8 : 1 | 75 | 34.0 | 55.0 | 11.0 |
| 112 | 314 | 730 | 1 : 1 | 11 | 51.7 | 41.0 | 7.3 |
| 122 | 314 | 410 | 0.95 : 1 | 42 | 47.9 | 40.5 | 11.6 |
| 94 | 310 | 318 | 3.8 : 1 | 85 | 89.0 | 11.0 | — |
| 114 | 310 | 600 | 3.9 : 1 | 28 | 84.7 | 15.3 | — |
| 95 | 310 | 300 | 1.39 : 1 | 57 | 69.5 | 24.7 | 5.8 |
| 96 | 317 | 360 | 1.47 : 1 | 28 | 69.6 | 26.9 | 3.5 |
| 98 | 320 | 340 | 1.16 : 1 | 37 | 53.5 | 38.4 | 8.1 |

It is proper to note here that, according to the data published by Taft and Stratton[5], during the photochemical chlorination of isobutane the reaction proceeds to a considerable extent on the surface of the reaction vessel, on which the concentration of reactants is higher than in the gas phase. According to the recent data of Chambers and Ubbelohde, [6], during chlorination of $C_5$ - $C_7$ paraffinic hydrocarbons by treatment with certain reagents an effect analogous to that of the reaction tube filled with inert packing occurs on the surface of the reaction vessel.

Influence of space rate and ratio of reactants on product yield in the thermal chlorination of propane. The influence of space rate on product yield in the thermal chlorination of propane was studied at a temperature of 300°; the space rate was varied from 11 to 85 hours$^{-1}$. The data are presented in Table 2.

As seen from the table, variation of the space rate within the limits studied had little effect on the ratios among the chloropropanes of differing degrees of substitution. These ratios depended on the composition of the reacting mixture.

The experimental data obtained during the study of the effect on product composition of propane-to-chlorine ratio are presented in Figure 2. As would be expected, an increase in molar excess of hydrocarbon in the re-

. action mixture led to a decrease in the yields of di- and trichloro substituted propanes.

Influence of reaction temperature on the yield of products from the chlorination of propane. The influence of temperature on the content of mono- and polychloropropanes in the reaction products, is shown in Table 3.

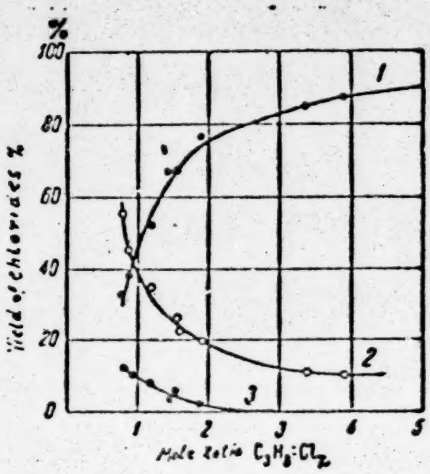


Fig. 2. Influence of $C_3H_8$: $Cl_2$ ratio on the composition of the chlorination products. 1) Monochloropropanes; 2) dichloropropanes; 3) trichloropropanes.

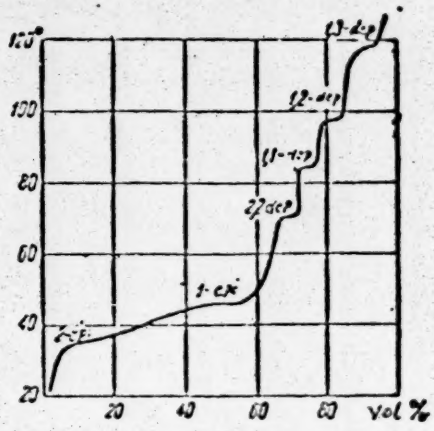


Fig. 3. Distillation curves for the products of the thermal chlorination of propane. Temperature 314°. Mole ratio, $C_3H_8$: $Cl_2$ 0.95: 1. cp-chloropropane; dcp-dichloropropane.

As seen from the data of Table 3, at a comparatively high excess of hydrocarbon in the reaction mixture (4: 1), temperature had almost no effect on the ratio between mono- and dichloro derivatives. At a lower excess of hydrocarbon (2: 1), an increase in temperature led to some increase in the yield of dichloro derivatives. The ratio between 1- and 2-monochloropropane and the physicochemical properties of these compounds are given in Table 4.

Literature data for 2-chloropropane are: $n_D^{20}$ 1.3770, $d_4^{20}$ 0.8617; for 1-chloropropane $n_D^{20}$ 1.3886; $d_4^{20}$ 0.8923. The dichloropropanes obtained contained all possible isomers, as may be seen from the distillation curve presented in Figure 3 (obtained in a column with glass packing, equivalent to 22 theoretical plates). The dichloropropanes were not investigated in greater detail.

TABLE 3

| Experiment No. | Temp., °C | Mole ratio $C_3H_8$: $Cl_2$ | Product composition, weight % | | |
|---|---|---|---|---|---|
| | | | Monochloro-propanes | Dichloropropanes | Trichloropropanes |
| 90 | 315 | 1.9 : 1 | 73.1 | 22.7 | 4.2 |
| 91 | 310 | 1.9 : 1 | 78.2 | 20.2 | 1.5 |
| 117 | 350 | 2 : 1 | 58.0 | 34.3 | 7.7 |
| 118 | 398 | 2 : 1 | 61.2 | 31.3 | 7.5 |
| 121 | 315 | 3.57 : 1 | 82.1 | 17.7 | – |
| 123 | 400 | 3.6 : 1 | 81.2 | 18.8 | – |
| 178 | 300 | 4 : 1 | 83.9 | 16.1 | – |
| 179 | 350 | 4 : 1 | 83.8 | 16.2 | – |
| 180 | 400 | 4 : 1 | 83.9 | 16.1 | – |

TABLE 4

| Temp., °C | Mole ratio $C_3H_6$ : $Cl_2$ | Composition of monochloropropanes | | Properties of 2-chloropropane | | Properties of 1-chloropropane | |
|---|---|---|---|---|---|---|---|
| | | 2 | 1 | $n_D^{20}$ | $d_4^{20}$ | $n_D^{20}$ | $d_4^{20}$ |
| 300 | 4 : 1 | 42.8 | 57.2 | 1.3772 | 0.8647 | 1.3884 | 0.8936 |

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Received October 19,1955



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# THE RULE OF AUWERS-SKITA AND THE PROPERTIES OF STEREOISOMERIC 1,4-DI-ISOPROPYLCYCLOHEXANES

A. L. Liberman, T. V. Lapshina and Academ cian B. A. Kazansky

During the synthesis of dialkylcycloalkanes, there is usually formed a mixture of cis- and trans-isomers, the separation of which frequently presents considerable difficulty in view of the closeness of their boiling points. In no case does the difference in boiling points of a pair of stereoisomers exceed 8°, and more frequently it is considerably less, dropping in some instances to a few tenths of a degree. Therefore, a total of only 14 dialkylcycloalkanes has been separated into the individual stereoisomers up to the present [1-7].

One of the most important problems in the study of the stereoisomers of cycloalkanes is the answer to the question as to which of a given pair of compounds should be assigned the cis- or trans-form. Usually, to answer this question use is made of the Rule of Auwers-Skita, according to which the trans-form of a dialkylcycloalkane has a lower boiling point, index of refraction, and specific gravity but a higher molar refraction than the cis-form. In recent years this rule has been subjected to review; it has been shown that it does not apply to 1,3-dimethylcyclohexanes, and that in this case the cis-form possesses those properties which, according to the Rule of Auwers-Skita, should belong to the trans-form [8]. In a recent communication it was shown that this is also true for 1,3-dimethylcyclopentane [9].

It should be noted that the Rule of Auwers-Skita is based on examples at the boundary of an unlimited number of cases of stereoisomers, chiefly on the first members of different homologous series of cyclic compounds, and as yet there are no data as to how it applies to higher molecular weight homologs. This communication is concerned with one exception to this rule.

By hydrogenating very pure 1,4-diisopropylbenzene, we prepared a mixture of 1,4-diisopropylcyclchexanes which was separated into the stereoisomers; the purity of each of these was 99.6-99.7%.

It was completely unexpected that, contrary to the rule of Auwers-Skita, the lower boiling isomer had the higher index of refraction and specific gravity and the lower molar refraction; that is, it had all the properties which should, according to this rule, belong to the cis-isomer, except boiling point. Moreover, it had the lower freezing point, which is also characteristic of the cis-form. The higher boiling isomer had, accordingly, the lower constants. Each of them were subjected separately to catalytic dehydrogenation and formed 1,4-diisopropylbenzene which did not exhibit freezing point depression when mixed with a sample of a pure preparation of this hydrocarbon. Thus, both stereoisomeric forms were structurally identical.

Comparison of the Raman spectra of these stereoisomers with spectra of known stereoisomeric 1,4-dialkylcyclohexanes • showed that the spectrum of the lower boiling isomer was of a frequency characteristic of cis-1,4-dialkylcyclohexanes, and the spectrum of the higher boiling compound had a frequency characteristic of the trans-form (see Table 1).

It should be noted that recently S. D. Mekhtiev and co-workers published a communication on their preparation of the stereoisomeric diisopropylcyclohexanes which had the following properties: trans-isomer, b.p. 60°/7 mm, $n_D^{20}$ 1.4480, $d_4^{20}$ 0.8145; cis-isomers, b.p. 65°/7 mm, $n_D^{20}$ 1.4498, $d_4^{20}$ 0.8192. These properties differ considerably from those obtained for our preparations (see below). Unfortunately, the properties of the 1,4-diisopropylbenzene which these authors used in the synthesis of their compounds (b.p. 204-206°, $n_D^{20}$ 1.4922, $d_4^{20}$ 0.8572), also differed considerably from the properties cited by Newton [12] (b.p. 210.3/760 mm, $n_D^{20}$ 1.4895, $d_4^{20}$ 0.8571) and by Melpolder [13] (b.p. 210.37°/760 mm, freezing point 17.07° $n_D^{20}$ 1.48983, $d_4^{20}$ 0.85676) for their preparations of this hydrocarbon, moreover, the preparation of Melpolder had a purity of 99.8 %. Unfortunately, S. D. Mekhtiev and co-workers did

• The Raman spectra of stereoisomeric 1,4-dimethylcyclohexanes were studied earlier [10]; spectra of 1-methyl-4-ethyl- and 1,4-diisopropylcyclohexanes were determined by V. T. Aleksanyan, P. A. Bazhulin and Kh. E. Sterin, to whom we express our appreciation.

not give the freezing point of their starting material, which would have made it possible to judge its purity.

Thus the significant difference in properties published in the article by Mekhtiev and co-workers and those presented by Newton and by Melpolder, and cited in the present work, forces us to regard the results obtained by S. D. Mekhtiev as unreliable.

TABLE 1

Characteristic Frequencies of Stereoisomeric 1,4-Dialkylcyclohexanes

| | Cis | Trans |
|---|---|---|
| 1,4-Dimethylcyclohexane | 637 (18) | 760 (150) |
| 1-Methyl-4-ethylcyclohexane | 631 (34) | 754 (80) |
| Lower boiling 1,4-diisopropylcyclohexane | 629 (46) | – |
| Higher boiling 1,4-diisopropylcyclohexane | – | 758 (39) |
| | – | 766 (50) |

## EXPERIMENTAL

1,4-Diisopropylbenzene. Technical diisopropylbenzene and 202-206° and 202-210° fractions isolated from technical diisopropylbenzene** were distilled under vacuum in a column of 25 theoretical plates, and the fraction boiling at 90.7-101.7/ 18.5 mm was collected (2.22 kg, $n_D^{20}$ = 1.4835). This fraction was subjected to sulfonation with freshly prepared 2% oleum using 2/3 volume per volume of hydrocarbon. With this ratio of reagents, the sulfonic acids separated as a separate layer between the unreacted hydrocarbon and the layer of sulfuric acid. The separated sulfonic acids, to which was added 50 ml $H_2SO_4$, were subjected to hydrolysis by steam. Fractions were collected in relation to the temperature of the reaction mass. The first fraction distilled over at a temperature of the reaction mass of 99-100°; it contained 70-90% diisopropylbenzene (500 g). From the succeeding fractions, 214 g of the same distillate was obtained by a second sulfonation and hydrolysis. Final purification was carried out by recrystallization from ether. The mixture of hydrocarbon and ether (mole for mole) was chilled in a beaker to −60°, and the liquid phase was removed by filtration [14]. If the freezing point of the vacuum distilled hydrocarbon was lower than −17.2°, it was recrystallized again. Thus, 318.5 g of hydrocarbon was obtained which, after distillation in a column of 83 theoretical plates, had the properties: b.p. 96.5°/ 18 mm, freezing point −17.1°, $n_D^{20}$ 1.4900, $d_4^{20}$ 0.85679. These properties are practically indistinguishable from the data of Melpolder [13] cited above.

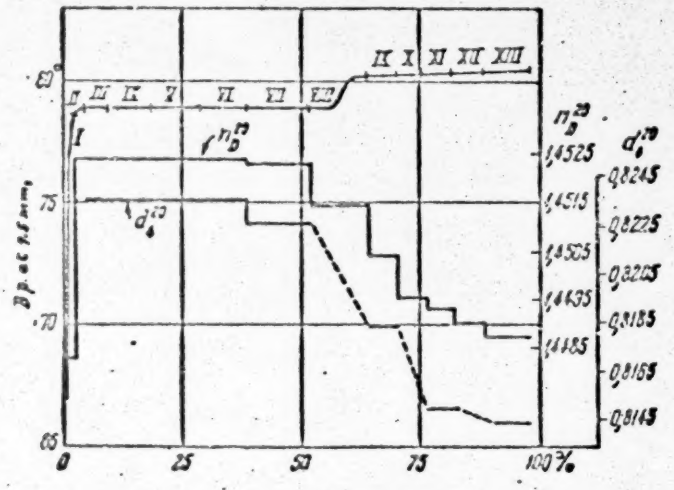


Fig. 1. Distillation curve of the stereoisomeric 1,4-diisopropylcyclohexanes.

Preparation of the stereoisomeric 1,4-diisopropylcyclohexanes. Leached Raney nickel was mixed with heptane in a Wurtz flask, and the latter was distilled to complete removal of the water from the catalyst. The anhydrous catalyst and 150 g of 1,4-diisopropylbenzene were charged to an 0.75-liter autoclave. Absorption of hydrogen

** We take this opportunity to express our appreciation to Yu. G. Mamedaliev, active member of the Academy of Science AzSSR, for kindly giving us the fractions.

(90-100 atm initial pressure) proceeded very fast at 190°. After distillation of the heptane, and chromatographing with silica gel, there was obtained 133.2 g of 1,4-diisopropylcyclohexane with $n_D^{20}$ 1.4511. The results of the distillation of 132.8 g of this preparation in a column of 100 theoretical plates are presented in Figure 1. Fractions III-VI did not differ in constants except for small differences in freezing points. Judging by the latter, Fraction IV was purest preparation of cis-1,4-diisopropylcyclohexane. The freezing point curve of this fraction is presented in Figure 2. The cryoscopic constant of the cis-form was found by a determination of the freezing point of a mixture of this hydrocarbon with 1.29% trans-form. It was 0.0070 mole/degree. From the course of the freezing point curve and the cryoscopic constant, it follows that the purity of the cis-1,4-diisopropylcyclohexane was 99.7%.

Properties of cis-1,4-diisopropylcyclohexane: b.p., 78.9°/7.5 mm; freezing point, −52.9°; $n_D^{20}$ 1.4524; $d_4^{20}$ 0.8236; $MR_D$ 55.17; calculated $MR_D$ 55.42.

Trans-1,4-diisopropylcyclohexane was not obtained in a pure form by this distillation, as is evident from the progression of the constants in Fractions IX - XIII (see Figure 1). Therefore, Fractions X-XIII were combined and redistilled in the same column but at a higher reflux ratio. In this manner, after separation of the leading fraction, there was obtained 19.6 g of trans-1,3-diisopropylcyclohexane. The residue in the flask did not differ from it in constants. The freezing point curve of trans-1,4-diisopropylcyclohexane is presented in Figure 3*. Its cryoscopic constant was found by the determination of the freezing point of a mixture of this hydrocarbon with 1.15% cis-form. It was 0.0430 mole/degree. From the course of the freezing point curve and the cryoscopic constant, it follows that the purity of the trans-1,4-diisopropylcyclohexane was 99.6%.

Properties of trans-1,4-diisopropylcyclohexane: b.p., 80.4°/7.5 mm; freezing point, −28.0°; $n_D^{20}$ 1.4485; $d_4^{20}$ 0.8143; $MR_D$ 55.38; calculated $MR_D$ 55.42.

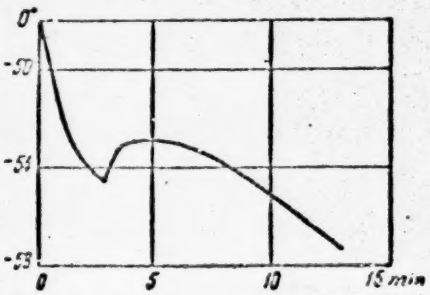


Fig. 2. Freezing point curve for cis-1,4-diisopropylcyclohexane.

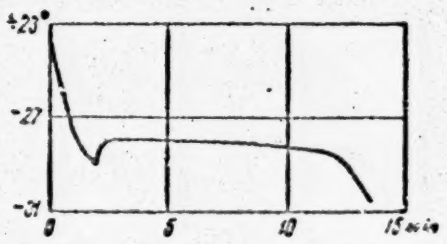


Fig. 3. Freezing point curve for trans-1,4-diisopropylcyclohexane.

Dehydrocenation of the stereoisomeric 1,4-diisopropylcyclohexanes. a) 10.8 g of cis-1,4-diisopropylcyclohexane was passed at 303° and a space rate of 0.8 liter per liter of catalyst per hour over 10 cc of platinized carbon. 8.1 g of catalyzate was collected: $n_D^{20}$ 1.4884; freezing point, −21.7°. A mixture of it with an equal volume of known 1,4-diisopropylbenzene (freezing point, −17.2°) had a freezing point of −19.2°.

b) 6.8 g of trans-1,4-diisopropylcyclohexane was passed at 300° and a space rate of 0.5 liter per liter of catalyst per hour over 10 cc of platinized carbon. 5.6 g of catalyzate was collected: $n_D^{20}$ 1.4894; freezing point, −27.3°. A mixture with an equal volume of 1,4-diisopropylbenzene had a freezing point of −20.8°.

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Received November 5, 1955

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# EXPERIMENTAL STUDY OF EQUILIBRIUM CONDITIONS DURING THE REACTION OF ZINC OXIDE WITH ZINC SULFIDE

A. L. Okunev and L. A. Popovkina

(Presented by Academican A. M. Frumkin, November 5,1955)

Equilibrium conditions during the reaction of zinc oxide and zinc sulfide have not been studied experimentally. This reaction has great practical significance in the analysis of questions connected with the recovery of zinc by the pyrometallurgical processes of the complex processing of copper-zinc ores and concentrates. Calculated data [1] have been used in the past for this purpose.

The results of an experimental study of equilibrium conditions for the reaction

$$2ZnO\,(solid) + ZnS\,(solid) = 3Zn\,(gas) + SO_2\,(gas) \qquad (a)$$

are briefly reported in the present communication, and are compared with calculated data.

The thermodynamic analysis of Reaction (a) was carried out by the exact differential method [2] using the thermodynamic data [3-5] presented in Table 1. The results of the calculations are presented in Table 2.

TABLE 1

Funcamental Thermodynamic Data

| Substance | $\Delta H_{298}$ | $S_{298}$ | Specific heat equation | Source |
|---|---|---|---|---|
| Zn (gas) | 31200 | 38.46 | $c_p = 4.97$ | [3] |
| $SO_2$ | −70940 | 59.4 | $c_p = 13.35 + 0.22\cdot10^{-3}T - 6.65\cdot10^{5}T^{-2}$ (0.2 %, 400 − 2500° K) | [3,5] |
| ZnO | −82540 | 10.4 | $c_p = 11.71 + 1.22\cdot10^{-3}T - 2.18\cdot10^{5}T^{-2}$ (12.098-16000° K) | [3,4] |
| ZnS | −48400 | 13.8 | $c_p = 12.16 + 1.24\cdot10^{-3}T - 1.36\cdot10^{5}T^{-2}$ (3%, 298-1200° K) | [3,4] |
| $(ZnS)_\alpha \longrightarrow (ZnS)_\beta$ | 3200 | – | – | – |

TABLE 2

Calculated change in isobaric thermodynamic potential, equilibrium constant, and equilibrium values of $P_{Zn}$ for Reaction (a)

| T, °K | $\Delta F^\circ_T$ | log K | $P_{Zn}$ |
|---|---|---|---|
| 1273 | 66010 | −11.32 | $1.91\cdot10^{-3}$ |
| 1373 | 53652 | − 8.53 | $9.75\cdot10^{-3}$ |
| 1473 | 41750 | − 6.18 | $3.74\cdot10^{-2}$ |
| 1573 | 29273 | − 4.07 | $1.26\cdot10^{-1}$ |

The experimental study of equilibrium conditions for Reaction (a) was carried out by passing a neutral gas (purified nitrogen) over the reaction mixture of chemically pure, crystalline ZnO and ZnS, which were taken in stoichiometric ratio. The reaction tube and the nitrogen rate were selected so that the composition of the gas phase corresponded to equilibrium. The nitrogen rate was 5 liters per hour. The experiments were carried out at 1000 1200° C. Duration of the experiments was 30 minutes. The equilibrium composition of the gases was determined by the decrease in weight of the weighted sample.

Since cooling of the gas mixture reverses Reaction (a), quenching of the gas mixture is not suitable as a method for determining the equilibrium composition of the gases. Other possible methods, as, for example, absorption of the

zinc vapors by some absorbent, are characterized by great complexity of experimental procedure.

The experimental data and the values calculated from them for equilibrium constants for Reaction (a), changes in isobaric thermodynamic potential, and $P_{Zn}$ at the temperatures of the experiments are presented in Table 3.

TABLE 3

Change in Isobaric Thermodynamic Potential, Equilibrium Constant, and Equilibium Values of $P_{Zn}$ for Reaction (a) from Experimental Data.

| T, °C | Loss in weight mg/ min. | $\Delta F^\circ_T$ | log K | $P_{Zn}$ | $\Delta F^\circ_T$ | log K | $P_{Zn}$ |
|---|---|---|---|---|---|---|---|
| | | Without correction for side reactions | | | Taking side reactions into consideration | | |
| 1000 | 1.093 | 60400 | −10.359 | $3.40 \cdot 10^{-3}$ | 61000 | −10.477 | $3.14 \cdot 10^{-3}$ |
| 1100 | 4.06 | 50800 | − 8.077 | $1.26 \cdot 10^{-2}$ | 51100 | − 8.133 | $1.22 \cdot 10^{-2}$ |
| 1200 | 14.16 | 39700 | − 5.891 | $4.40 \cdot 10^{-2}$ | 39850 | − 5.920 | $4.35 \cdot 10^{-2}$ |

In calculating the values of $\Delta F^\circ_T$, log K, and $P_{Zn}$, it was necessary to evaluate the influence of other processes taking place along with Reaction (a), for example:

$$ZnO\,(solid) = ZnO\,(gas); \quad (b)$$
$$ZnO\,(solid) = ZnS\,(gas) + {}^1/_2\,O_2\,(gas); \quad (c)$$
$$ZnS\,(solid) = ZnS\,(gas); \quad (d)$$
$$ZnS\,(solid) = Zn + {}^1/_2\,S_2\,(gas). \quad (e)$$

The sublimation and dissociation pressures of zinc oxide are many times less than the corresponding pressures for zinc sulfide. Therefore, it is sufficient to consider processes (d) and (e) in evaluating the influence of the above processes on Reaction (a). Their influence can be taken into account by proceeding from the experimental data on the sublimation and dissociation of zinc sulfide [6]. In the latter case, the evaluation must be carried out taking into account the equilibrium value of $P_{Zn}$ for Reaction (a).

Values of $\Delta F^\circ_T$, log K and $P_{Zn}$ calculated taking into account processes (d) and (e) are also presented in Table 2. Comparison of these values with the corresponding values calculated without considering the side reactions shows that the yields of products from side reactions were within experimental error, and that their influence at temperatures above 1100° can be neglected.

The experimental and calculated data are in satisfactory agreement, especially above 1100°C. However, in all cases the experimental data were somewhat higher than those obtained by calculation.

The enthalpy change at 293° K for Reaction (a) as calculated from the experimental data was 216,000 cal., against 233,000 cal. from calorimetric measurements. The enthalpy change for Reaction (a) in the temperature range 1000-1200° was 204,830 cal., and the entropy change was 112.0 e.u.

The experimental data are satisfactorily expressed by the equations:

$$\Delta F^\circ_T = 204880 - 112.0\,T; \qquad \log K = \frac{44782}{T} + 24.481;$$
$$P_{Zn} = \frac{11195.5}{T} + 6.12.$$

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Received April 4, 1955



Ural Research and Development Institute for the Copper Industry

# THE DIRECT SYNTHESIS OF ALKYL- AND ALKENYLCHLOROSILANES FROM 1,1--DICHLOROETHANE AND 2,2-DICHLOROPROPANE

Associate Member of the Academy of Science USSR A. D. Petrov, S. I. Sadykhzade and I. L. Tsetlin

Direct synthesis from methylene dichloride [dichloromethane], as is known [1], leads to the formation of only saturated products: 1) hexachlorodisilylmethane ($Cl_3Si-CH_2-SiCl_3$) and 2) 1,1,3,3,5,5-hexachlorotrimethylenesilane ($[CH_2 \cdot SiCl_2]_3$). It seemed of interest to carry out the direct synthesis using the closest homologs of methylene dichloride – the asymmetrical dichloride: methylmethylene dichloride (1,1-dichloroethane) and dimethylmethylene dichloride (2,2-dichloropropane), since here, besides obtaining analogs of the above-mentioned saturated products, one might also expect the formation of alkenylchlorosilanes as a consequence of the probable splitting off of HCl. Our expectation was completely justified: 20-25% of the condensate consisted of vinyl (isopropenyl)chlorosilanes. 35-45% of penta- and hexachloroethanes (propanes). The yield of the cyclic forms $(CH_3-CH \cdot SiCl_2)_3$ and $[(CH_3)_2 \cdot C \cdot SiCl_2]_3$ was negligibly small.

Using, for the first time in the direct synthesis, a circulating type apparatus, 1740 g of $CH_3 \cdot CHCl_2$ were circulated over a Si-Cu (80:20) alloy at 360-380° for 16 hours. 445 g of condensate was obtained. From distillation data presented in Table 1, it is seen that the condensate had the composition: 4.5% $SiCl_4$; 15.2% unreacted $CH_3 \cdot CHCl_2$, 6.4% vinyldichlorosilane, $Cl_2HSiCH=CH_2$ 16% vinyltrichlorosilane, $Cl_3Si-CH=CH_2$, 6.5% 1,1-bis-dichlorosilylethane, ($Cl_2$ 18.5 $Cl_3 \cdot CH \cdot CH_3$ 18.5% 1-dichlorosilyl-1-trichlorosilylethane, $(Cl_2HSi)(Cl_3Si) \cdot CH-CH_3$, 18.5% 1,1-bis(trichlorosilyl)ethane $(Cl_3Si)_2 \cdot CH-CH_3$. 500 g of $CH_3 \cdot CCl_2 \cdot CH_3$ were passed over Si–Cu at 360-350° for 25 hours. 240 g of condensate were obtained, the distillation data for which are presented in Table 2. From the distillation data, it is seen that the condensate had the composition 2% $SiCl_4$, 15% unreacted $CH_3 \cdot CCl_2 \cdot CH_3$; 7.6% dichloroisopropenylsilane,

TABLE 1

Alkyl- and Alkenylchlorosilanes from $CH_3-CHCl_2$

| Compound | B.p., °C | Press in mm Hg | $d_4^{20}$ | $n_D^{20}$ | Found/calculated, % | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | H | C | Si | Cl |
| $Cl_2HSi-CH=CH_2$ | 72-73 | 750.5 | 1.1222 | 1.4160 | 3.25<br>3.10 | 18.54<br>18.88 | 21.85<br>22.03 | – |
| $Cl_2Si-CH=CH_2$ | 92.5 | 750.5 | 1.2426 | 1.4295 | – | – | – | – |
| $CH_3-CH(SiHCl_2)(SiHCl_2)$* | 165.5 | 750.5 | 1.3043 | 1.4578 | 2.56<br>2.63 | 10.91<br>10.53 | 25.36<br>24.56 | – |
| $CH_3-CH(SiHCl_2)(SiCl_3)$ | 181 | 750.5 | 1.4310 | 1.4740 | 1.69<br>1.90 | 9.34<br>9.14 | 21.34<br>21.33 | 67.94<br>67.61 |
| $CH_3-CH(SiCl_3)_2$ | 197.5 | 750.5 | 1.5059 | 1.4820 | 1.43<br>1.34 | 8.34<br>8.08 | 19.11<br>18.89 | 71.01<br>71.71 |
| $CH_3-CH[SiH(CH_3)_2]_2$* | 124 | 746 | 0.7597 | 1.4252 | 12.33<br>12.40 | 50.23<br>49.3 | – | – |
| $CH_3 \cdot CHSiH(CH_3)_2$* $\cdot Si(CH_3)_3$* | 140 | 733.5 | 0.7756 | 1.4288 | 12.53<br>12.50 | 52.58<br>52.50 | 34.76<br>35.0 | – |
| $CH_2 \cdot CH[Si(CH_3)_3]_2$* | 155.7 | 733 | 0.7821 | 1.4340 | 12.60<br>12.64 | 55.37<br>55.17 | 32.05<br>32.18 | – |

* First obtained compound

$Cl_2HSi-\underset{\underset{CH_3}{|}}{C}=CH_2$, 10.1% isopropenyltrichlorosilane; $Cl_3Si-\underset{\underset{CH_3}{|}}{C}=CH_2$, 14% 2,2-bis(dichlorosilyl)propane, $(Cl_2HSi)_2\cdot C\cdot(CH_3)_2$; 11.5% 2-dichlorosilyl-2-trichlorosilyl propane, $(Cl_2HSi-C(CH_3)_2\cdot SiCl_3$; 8.5% 2,2-bis-(trichlorosilyl)propane, $(Cl_3Si)_2\cdot C(CH_3)_2$.

**TABLE 2**

Alkyl- and Alkenylsilanes from $CH_3-CCl_2-CH_3$

| Compound | B.p. in °C at 758 mm | $d_4^{20}$ | $n_D^{20}$ | Found/calculated, % | | | |
|---|---|---|---|---|---|---|---|
| | | | | H | C | Si | Cl |
| $Cl_2HSi-\underset{\underset{CH_3}{|}}{C}=CH_2$* | 90 | 1.0787 | 1.4310 | – | – | 20.11<br>19.85 | – |
| $Cl_3Si-\underset{\underset{CH_3}{|}}{C}=CH_2$ | 113 | 1.2398 | 1.4412 | – | – | – | – |
| $(CH_3)_2\cdot C(SiHCl_2)_2$* | 175.8 | 1.2635 | 1.4709 | – | – | – | – |
| $(CH_3)_2\cdot C\cdot(HSiCl_2)(SiCl_3)$* | 195.5 | 1.3808 | 1.4818 | 12.8<br>12.9 | 3.01<br>2.48 | 20.5<br>20.3 | 63.4<br>64.2 |
| $(CH_3)_2\cdot C\cdot(SiCl_3)_2$ | 214 | 1.3733 | 1.4927 | – | – | 18.05<br>16.0 | – |
| $(CH_3)_2\cdot C\cdot[SiH(CH_3)_2]_2$ | 142-143 | 0.7779 | 1.4360 | 12.55<br>13.3 | 53.26<br>52.5 | – | – |
| $(CH_3)_2\cdot C\cdot[SiH(CH_3)_2\cdot Si(CH_3)_3]$* | 159-160 | 0.7939 | 1.4378 | 12.69<br>12.74 | 55.36<br>55.05 | – | – |

* First obtained compound

Moreover, a small amount of white crystals with a melting point of 83-90° were isolated which according to the analytical data, had the formula $[SiCl_2\cdot C(CH_3)_2]_3$. As can be seen, the yield of alkenylsilanes, in particular vinyltrichlorosilane, considerably exceeded the yield of the latter compound when prepared by direct synthesis from $CH_2=CHCl$ [2]. As regards isopropenylchlorosilanes, these compounds were not generally obtained in the direct synthesis. The formation of alkenylsilanes can be represented, therefore, both as a direct synthesis from vinyl and isopropenyl chlorides, which takes place at the moment of formation of the latter with higher yields, and by splitting off HCl from the initially formed chloroalkyltrichlorosilanes:

$$CH_3-CHCl_2 \begin{cases} \xrightarrow{+\,Si-Cu} CH_2=CHSiCl_3 \\ \longrightarrow CH_3-CHCl\cdot SiCl_3 \xrightarrow{-HCl} CH_2=CHSiCl_3 \end{cases}$$

$$CH_3-\underset{\underset{CH_3}{|}}{C}-Cl_2 \begin{cases} \xrightarrow{+\,Si-Cu} CH_2=\underset{\underset{CH_3}{|}}{C}\cdot Cl \xrightarrow{+\,Si-Cu} CH_2=\underset{\underset{CH_3}{|}}{C}\cdot SiCl_3 \\ \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{C}Cl\cdot SiCl_3 \xrightarrow{-HCl} CH_2=\underset{\underset{CH_3}{|}}{C}\cdot SiCl_3 \end{cases}$$

Thus, here for the first time it has been shown that asymmetrical dichlorides can react with silica using both one and two atoms of chlorine.

An experiment conducted by passing 1,2-dichloroethane, under the same conditions, over the catalyst at 450° did not yield vinylchlorosilanes.

The ability of unsaturated asymmetrical dichlorides to react both one and two atoms of chlorine has already been demonstrated by S. I. Sadykhzade and A. D. Petrov [3] in the case of 1,3-dichlorobutene-2 which formed both $Cl_3Si-CH_2-CH=CCl-CH_3$ and $Cl_3SiCH_2-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-SiCl_3$.

It is impossible to exclude the possibility that α-chloroalkyltrichlorosilanes are intermediate products on the road to the formation of penta- and hexachloroethanes (propanes). Recently, S. I. Sadykhzade, E. A. Chernyshev and V. F. Mironov [4] showed that α- and β-mono- and dichloroalkyltrichlorosilanes can be used in the direct synthesis of di- and polysilanechlorides.

## EXPERIMENTAL

1,1-Dichloroethane, b.p. 57°, was obtained by the action of $PCl_5$ on acetaldehyde, and 2,2-dichloropropane, b.p. 68°, was obtained by the action of the same reagent on acetone. A preliminary experiment, passing 250 g of 2,2-dichloropropane over Si-Cu at 280° at a rate of 25 g/hour, showed that, under these conditions, the main reaction is the splitting out of HCl with the formation of isopropenyl chloride, $CH_3CCl=CH_2$ and $SiCl_4$. On the assumption that an increase in temperature and a greater contact time with the catalyst were necessary for the formation of alkenylchlorosilanes, we changed the method of synthesis. The product obtained after a single pass over the catalyst was returned again to the flask and again passed over the catalyst heated to 360-380° (see Figure 1). The boiling point of the products, which were vaporized from the flask at the end of the experiment was increased to 100-110°. That Englisch, [5], with a single pass of 1,1-dichloroethane over the catalyst at 350-400°, obtained only one 1,1-bistrichlorosilylethane in a yield of 8% indicates the valuable expediency of our method of synthesis.

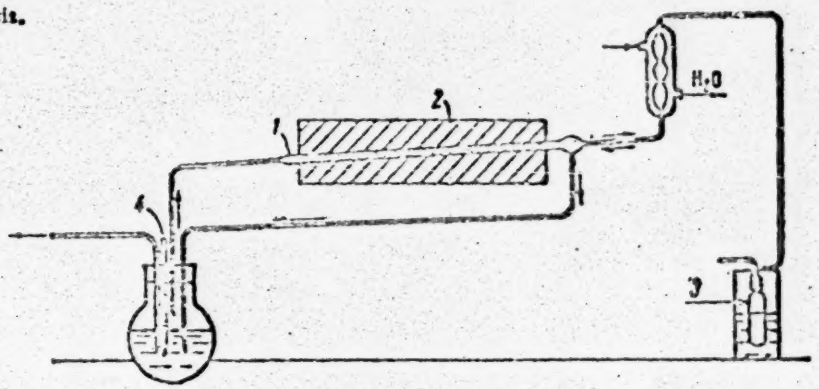


Fig. 1. Refractory glass tube filled with Si-Cu alloy; 2) tubular furnace; 3) trap; 4) thermometer.

The properties of the products of the synthesis obtained from 1,1-dichloroethane, and also of certain products of their alkylation, are presented in Table 1. The properties of the products of the synthesis from 2,2-dichloropropane and of certain products of their alkylation are presented in Table 2. The properties of the first isopropenyltrichlorosilane obtained by direct synthesis compare closely with the properties of this compound recently synthesized by the dehydrochlorination of β-chloroisopropyltrichlorosilane, which was obtained by the chlorination of isopropyltrichlorosilane [6].

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Received September 7, 1955

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# A NEW METHOD OF SNYTHESIS OF POLYENIC KETONES WITH CONJUGATED DOUBLE BONDS

Gl. I. Samokhvalov, M. A. Miropolskaya and N. A. Preobrazhensky

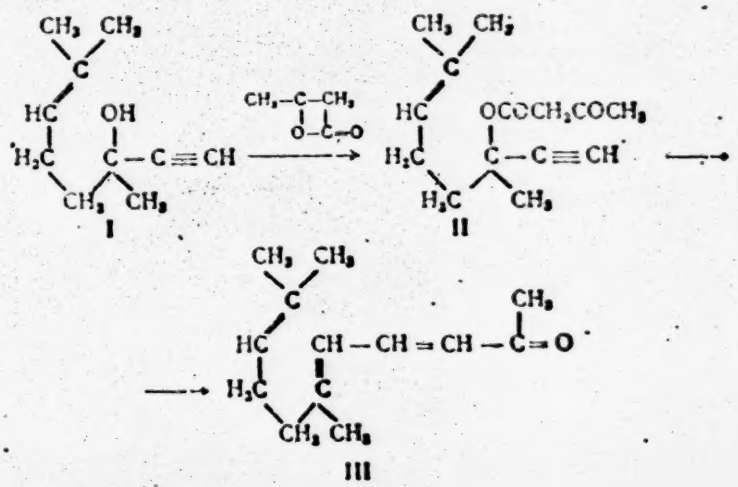
(Presented by Academician I. L. Knunyants, December 31,1955)

In 1940, it was noted that upon warming unsaturated ethylenic alcohols with acetoacetic ester, along with acylation, the formation of a certain amount of ketone also took place [1]. The ketone, contained a double bond which was separated from the carbonyl group by two methylene groups. In 1950, upon warming substituted ethylenic alcohols with esters of α-chloroacetoacetic ester, chloroketones were obtained, the treatment of which with pyridine lead to ketones with conjugated double bonds [2]. Recently, there appeared an indication that esters of acetoacetic acid with substituted ethylenic alcohols can be converted by hydrolysis into ketones [3].

We have established that acetylenic alcohols of the propargyl alcohol type are converted, with good yields, into esters of acetoacetic acid by the action of diketene. Raman spectra of the original alcohols and of the products of their reaction with diketene showed the characteristic frequency at 2112 $cm^{-1}$ for a triple bond. This showed that the terminal triple bond does not take part in the reaction with diketene. The esters prepared were distilled under vacuum without decomposition, and were obtained in the analytically pure state.

A distinguishing property of these esters is their ability, on heating to 160-170°, to undergo intramolecular rearrangement with the liberation of carbon dioxide and the formation of an unsaturated ketone. Instead of a weak u.v. absorption band at 245 mμ, characteristic of esters of acetoacetic acid, upon heating a strong absorption band appears which corresponds to conjugation of the carbonyl group with two double bonds.

Thus, for example, from the product of the condensation of methylheptenone with acetylene (I) we obtained pseudoionone (III):



The reaction is tied in with the participation of a methylene group and subsequent prototropic rearrangement of the thus formed allenic system of bonds. This series of reactions represents a new method for the synthesis of ketones with conjugated double bond systems.

3,7-Dimethyl-6-octen-1-yn-3-ol (I) was obtained by the condensation of 6-methylhepten-2-one with acetylene under the influence of metallic sodium in liquid ammonia solution. The yield was 74%. B.p. 83-84°/6mm; $n_D^{20}$ 1.4522; $d_4^{20}$ 0.8851; $M_D$ found 47.15; calculated $C_{10}H_{16}O$ [ ]$^3$ 47.43.

The ester with acetoacetic acid (II) was obtained by condensation of (I) with diketene under the influence of a catalytic amount of metallic sodium. The main fraction was isolated in 72% yield. B.p. 93-94°/0.2 mm; $n_D^{20}$ 1.4665; $d_4^{20}$ 0.9870; $M_D$ found 66.22; calculated $C_{14}H_{20}O_3$ [ ] 66.05.

Found %: C 71.42; H 8.64
Calculated %: C 71.18; H 8.47

Pseudoionone (III) was obtained by heating (II) in a stream of nitrogen at 160-170° for 3 hours. The material was distilled under vacuum. The main fraction was obtained in 61% yield. B.p. 90-92°/0.1 mm; $\lambda_{max}$ 290 mμ; $E_{1\%}^{1}$ cm 1030.

The 2,4-dinitrophenylhydrazone, m.p. 134-136°, was obtained by the action of a sulfuric acid solution of 2,4-dinitrophenylhydrazine.

Found %: N 14.83
$C_{15}H_{14}O_4N_4$. Calculated %: N 15.05

Upon decomposition of the mixture of isomers, the geometric isomer whose 2,4-dinitrophenylhydrazone melts at 147.5-148° predominated, and the isomer whose 2,3-dinitrophenylhydrazone melts at 119° was present only in traces. Thus essentially only one geometric isomer of pseudoionone, corresponding to an arrangement of substituents at the double bond of the geranial form of citral, was formed by the pyrolysis.

The authors express their appreciation to L. V. Lukyanova for obtaining and participating in the interpretation of the spectra.

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Received December 24, 1955

# SYNTHESES IN THE FIELD OF C – C DERIVATIVES OF CARBOHYDRATES

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(Presented by Academican A. I. Oparin, October 27, 1955)

Based on the work of previous investigations [1,2], we have carried out new syntheses of carbohydrate derivatives in which the substituent is joined directly to the sugar molecule by a carbon-carbon bond. In addition to derivatives of glucose (diphenyltetraacetylglucose and its brominated derivative and iodoanisyltetracetylglucose) and of xylose (thienyl-, diphenyl-, and allyltriacetylxylose), we prepared derivatives of still another sugar – galactose (anisyl-, phenetyl-, and diphenyltetraacetylgalactose). In addition, the possibility of preparing C – C derivatives of sugars, starting not with the acylated but with the methylated derivatives, was studied. Acylated carbohydrates have the disadvantage that during the reaction, a considerable part of the Grignard reagent is consumed by reaction with the acyl groups, which leads to a large amount of by-products. Methylated derivatives of sugars do not have this disadvantage but are less satisfactory in that they do not crystallize and distill only under fairly high vacuum.

In the preparation of the methylated derivatives of glucose, the glucose was converted into the methylglucoside, then, by the method of West and Holden [3], into pentamethylglucose, and, finally, into chlorotetramethylglucose [4]. As a result of these syntheses, anisyltetramethylglucose was prepared and isolated.

## EXPERIMENTAL

Thienyltriacetylxylose. This compound was prepared by the method used in the preparation of thienyltetraacetylglucose [1]. To the organomagnesium compound, prepared from 3.93 g (0.16 mole) of magnesium and 34.65 g (0.165 mole) of α-iodothiophene, was added 5 g (0.017 mole) of chloracetoxylose in ether, and the synthesis was carried out by the usual route. 2.1 g of raw product was isolated, which, upon recrystallization from gasoline (b.p. 110-115°) and isopropyl alcohol, formed white needles with a m.p. of 151-152°. This material is described here for the first time.

Found %: C 52.73; H 5.45
$C_{15}H_{18}O_7S$. Calculated %: C 52.62; H 5.30

Diphenyltetraacetylgalactose. The required pentaacetylgalactose was prepared by the method proposed by Hudson and Dale [5]. The pentaacetylgalactose was converted into chlorotetraacetylgalactose by the method of Freudenberg and Soff [6].

A solution of 38.5 g (0.16 mole) of 4-bromodiphenyl in 150 ml of absolute ether was added to activated magnesium iodide (4 g). The mixture was warmed on a water bath and stirred until the magnesium was dissolved. To this Grignard reagent was added 5 g (0.0136 mole) of chlorotetraacetylgalactose in 60 ml of absolute ether over a period of 30-40 minutes. The reaction mixture was boiled on the water bath for 4-5 hours with vigorous stirring. The decomposition and further treatment was carried out as in the synthesis of anisyltetraacetylglucose [1]. Evaporation of the ethereal solution gave the raw product which, upon recrystallization from isopropyl alcohol, gave lustrous crystals with a m.p. of 156-157°. The material is here described for the first time.

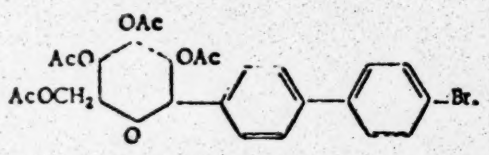
Found %: C 64.97; H 5.87
$C_{32}H_{32}O_9$. Calculated %: C 64.45; H 5.78

Diphenyltetraacetylglucose. This compound was prepared by the same method as the diphenyltetraacetylgalactose; crystallized from isopropyl or ethyl alcohol in the form of lustrous needles with a m.p. of 180°. The yield was 80 % of theory. The material is described here for the first time.

Found %: C 64.88; H 5.79
$C_{32}H_{32}O_9$. Calculated %: C 64.45; H 5.78

Bromodiphenyltetraacetylglucose. To 1 g (0.0023 mole) of diphenyltetraacetylgluco.. in 10 ml of carbon disulfide was added 1.5 g (0.009 mole) of bromine. The mixture was warmed on a water bath until the liberation of HBr ceased; the carbon disulfide was distilled off, and the residue was washed with 5% aqueous alkali. A slightly yellow oil was obtained which crystallized upon intimate mixing with petroleum ether. The material was purified by recrystallization from isopropyl alcohol. p- Bromodiphenyltetraacetylglucose with m.p. of 197° was obtained. The yield was 1.1 g (97% of theory). The structure was substantiated by oxidation with permanganate which gave p-bromophenylbenzoic acid with a m.p. of 193°.

It is obvious that the structure of the compound is:

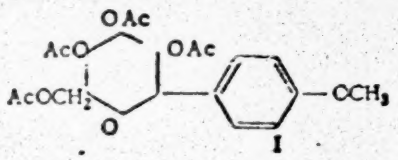



Diphenyltriacetylxylose*. This compound was obtained by the method described above. To the Grignard reagent, prepared from 3.93 g (0.16 mole) of magnesium and 38.5 g (0.165 mole) of p-bromodiphenyl, was added an ethereal solution of 5 g of chlorotriacetylxylose. After the usual treatment and recrystallization from gasoline there was obtained 0.5 g of white crystalline product melting at 191-192°.

| | | |
|---|---|---|
| | Found %: | C 67.40; H 6.16 |
| $C_{23}H_{24}O_7$. | Calculated%: | C 66.97; H 5.86 |

Iodoanisyltetraacetylglucose. To a solution of 1 g (0.002 mole) of anisyltetraacetylglucose in carbon tetrachloride was added dropwise with stirring and cooling a solution of 1.9 g of iodine chloride in a small amount of carbon tetrachloride. After 1 hour, the mixture was poured into water. The carbon tetrachloride layer was washed with a saturated solution of sodium bicarbonate, then with water, then dried over calcium chloride, and evaporated. The residue was recrystallized from isopropyl alcohol. Slightly yellow crystals melting at 151-153° were obtained. The yield was 38% of theory. This material is described here for the first time. 20.8% of iodine (calculated, 22.4%) was found by analysis. Upon oxidation with alkaline permanganate, p-methoxy-m-iodobenzoic acid melting at 230° was obtained.

The structure of the compound was:

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Anisyltetramethylglucose. To the organomagnesium compound, prepared from 0.99 g (0.041 mole) of magnesium and 8.4 g (0.045 mole) of p-bromoanisole, was gradually added dropwise with stirring a solution of 3.5 g (0.014 mole) of chlorotetramethylglucose in ether. After addition of the solution was completed, the mixture was warmed for another 2-3 hours, cooled and decomposed with water and acetic acid. The ethereal solution was separated, washed with a small amount of water, and dried over anhydrous sodium sulfate. The ether was distilled off. 1.5 g of anisyltetramethylglucose was obtained in the form of a thick, colorless syrup which, after oxidation with permanganate, gave anisic acid with a m.p. of 179-180°. This material is described here for the first time.

By the reaction of anisylmagnesium bromide with chlorotetraacetylgalactose, anisyltetraacetylgalactose, was prepared and isolated in the form of a syrup which, upon oxidation with permanganate, gave anisic acid. Phenetyltetraacetylgalactose, which gave ethoxybenzoic acid on oxidation, was prepared in the form of a syrup in an analogous manner. Allyltriacetylxylose was also obtained in the form of a colorless syrup.

* This compound was prepared in collaboration with A. S. Vishnyakov in the laboratory of the V. M. Molotov Rostov-on-the-Don State University.

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Received October 27, 1955

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# SYNTHESIS OF ALKYLFERROCENES

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Ferrocene (dicyclopentadienyl iron), first prepared in 1951 by Kealy and Pauson [1, 2], is a new type of organometallic compound with a new type of aromatic nucleus. Up to the present, a considerable number of cyclopentadienyl derivatives of various metals has been prepared [3]. In principle, the preparation of substituted ferrocenes and, in particular, ferrocene homologs from substituted cyclopentadienes is possible, but, in view of the poor availability of the latter, it has been necessary to prepare ferrocene derivatives, with few exceptions, from ferrocene itself [4-6].

At present, a series of direct substitution reactions of ferrocene is known: acylation [7], mercurization [8], metallation with lithium [8], arylation by means of diazo compounds [8, 9], and sulfonation [10] •. Ferrocenecarboxylic acids [8], haloferrocenes [11], and ferrocenylamines [12] have been prepared by means of secondary substitution. However, the simplest homologs of ferrocene have not been prepared up to the present.

Although ferrocene is easily acylated to acylferrocenes in the presence of aluminum chloride under the same conditions that benzene yields acylbenzenes, attempts to alkylate it have not been successful as yet. It is true that ferrocene has been successfully condensed with formaldehyde and with benzaldehyde in the presence of concentrated sulfuric acid [13] or anhydrous hydrogen fluoride [10], but the products of these reactions possess complex structures, and the simplest alkylferrocenes cannot be obtained by this route.

Since ketones of the ferrocene series are comparatively available, we have attempted to prepare homologs of ferrocene by reduction of the corresponding ketones.

Reduction of the ketones was carried out with a 10-fold excess of amalgamated zinc and concentrated hydrochloric acid in the presence of glacial acetic acid as a solvent. In all cases, the reaction was complete after 1 hour with little heating. After completion of the reaction, the reaction mixture was diluted with water, and the reaction product was extracted with benzene. The benzene solution was carefully washed with a solution of soda and water, after which the benzene was evaporated off. The resulting material was steam distilled in all cases except that of dibenzylferrocene, which would not steam distill. Final purification was by chromatography over aluminum oxide followed by washing with petroleum ether or vacuum distillation in a nitrogen atmosphere.

By this method, ethylferrocene was prepared from acetylferrocene [8] in a yield of 67 % of theoretical; the ethylferrocene was a reddish brown liquid with a sharp, camphor-like odor; b.p. 103-109° / 5.5 mm, $n_D^{19.5}$ 1.6017, $d_4^{19.5}$ 1.2469, MR 58.86.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 67.52; 67.76; | H 6.48; 6.57; | Fe 25.34; 25.12 |
| $C_{12}H_{14}Fe$. | Calculated %: | C 67.35; | H 6.54; | Fe 26.10 |

Diethylferrocene was prepared from diacetylferrocene [7] in a yield of 40-50% of theoretical; the diethylferrocene was a reddish brown liquid with a weaker odor than ethylferrocene; b.p. 123-124° / 5.5 mm, $n_D^{19}$ 1.5803, $d_4^{19}$ 1.1787, MR 69.89.

| | | | | |
|---|---|---|---|---|
| | Found %: | C 69.37; 69.28; | H 7.62; 7.68; | Fe 23.03; 23.04 |
| $C_{14}H_{18}Fe$. | Calculated %: | C 69.48; | H 7.43; | Fe 23.07 |

Diethylferrocene was also prepared in a yield of 48% of theoretical by E. G. Perevalova and R. V. Golovnya who hydrogenated diacetylferrocene over Raney nickel in ether at 200-260° and 220 atm. for 8 hours. The hydrogenation of diacetylferrocene was undertaken with the idea of splitting the five-membered ring to obtain ethylcyclopentane. This has now been accomplished under more vigorous conditions. Woodward has presented evidence to show that the acetyl groups in diacetylferrocene are on different cyclopentadienyl radicals. Consequently, similar positions

• Ferrocene diiminosulfonic acids have also been synthesized by the action of pyridine – sulfur trioxide on ferrocene (the method was developed by E. G. Perevalova).

are occupied by the ethyl groups in diethylferrocene and, probably, by the alkyl groups in the other compounds described herein.

Dipropylferrocene was prepared from dipropionylferrocene with a yield of 70% of theoretical; the dipropylferrocene was an orange-red liquid with a very weak odor; b.p. 137-138° / 5 mm, $n_D^{20}$ 1.5619, $d_4^{20}$ 1.1244, MR 77.91.

Found %: C 71.39; 71.24; H 8.03; 8.17; Fe 20.61; 20.63
$C_{16}H_{22}Fe$. Calculated %: C 71.17; H 8.14; Fe 20.68

Dibutylferrocene was prepared from dibutyrylferrocene with a yield of 60% of theoretical; the dibutylferrocene was an orange-red liquid with a weak odor; b.p. 164-165° / 6 mm, $n_D^{20}$ 1.5511, $d_4^{20}$ 1.1086, MR 85.75.

Found %: C 72.56; 72.50; H 8.80; 8.94; Fe 18.67; 18.64
$C_{18}H_{26}Fe$. Calculated %: C 72.55; H 8.72; Fe 18.73

The dibutylferrocene was steam distilled with difficulty.

Dibenzylferrocene was prepared from dibenzoylferrocene in a yield of 60% of theoretical; the dibenzylferrocene was a light yellow crystalline material with a m.p. of 101.5-102.5° after purification of chromatography and two-fold recrystallization from petroleum ether.

Found %: C 78.36; 78.60; H 5.90; 5.86; Fe 15.30; 15.34
$C_{24}H_{22}Fe$. Calculated %: C 78.73; H 6.00; Fe 15.25

The alkylferrocenes were very readily soluble in benzene, readily soluble in ether, slightly soluble in alcohol, and insoluble in water.

All the alkylferrocenes were easily oxidized by quinone in benzene solution, yielding alkylferricinium cations which could be extracted by hydrochloric acid. The blue, hydrochloric acid solutions containing cations of the investigated compounds were smoothly reduced by stannous chloride, giving the original alkylferrocenes.

The ethyl- and diethylferrocenes were extrememly prone to oxidize, and upon standing for several days they gradually deposited a residue. Dipropyl- and dibutylferrocenes were more stable, and dibenzylferrocene was completely undecomposed during storage.

It should be noted that the alkylferrocenes described in the present work belong to the, as yet, small group of liquid ferrocene compounds [11, 14]. The investigation of such compounds, the study of their physical properties, and particularly the determination of molar refraction and parachor are of special interest in the consideration of the type of bonds in ferrocene.

Dipropionylferrocene was prepared with a yield of 40% of theoretical by the reaction of 0.043 mole of ferrocene with 0.12 mole of propionyl chloride in the presence of 0.1 mole of aluminum chloride in 50 ml of carbon disulfide with mild warming for 30 minutes. The dipropionylferrocene was in the form of lustrous orange crystals with a m.p. of 53-54° after three recrystallizations from petroleum ether.

Found %: C 64.35; 64.48; H 6.05; 6.05; Fe 18.93; 18.84
$C_{16}H_{18}O_2Fe$. Calculated %: C 64.48; H 6.04; Fe 18.74

Di-n-butyrylferrocene was prepared by the same method from 0.048 mole of ferrocene, 0.1 mole of n-butyryl chloride, and 0.1 mole of aluminum chloride; the yield was 40%. It also was in the form of lustrous orange crystals with a m.p. of 74-75° after two recrystallizations from petroleum ether.

Found %: C 66.42; 66.58; H 6.91; 6.81; Fe 17.56; 17.79
$C_{18}H_{22}O_2Fe$. Calculated %: C 66.30; H 6.74; Fe 17.13

Dibenzoylferrocene * was prepared in a yield of 70 % of theoretical from 0.05 mole of ferrocene, 0.086 mole of benzoyl chloride, and 0.093 mole of aluminum chloride in carbon disulfide. It was a dark red crystalline material which crystallized from 50% aqueous alcohol and melted at 101-102°.

Dipropionylferrocene, similarly to acetyl- and diacetylferrocene, dissolved in concentrated hydrochloric acid giving it a dark violet-red color. Dibutyryl- and dibenzoylferrocene did not possess this property.

* Method developed by E. G. Perevalova.

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Received November 18, 1955



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# ALKYLATION OF CHLOROBENZENE WITH ISOPROPYL CHLORIDE IN THE PRESENCE OF $AlCl_3 \cdot HSO_4$ COMPLEX

Academician A. V. Topchiev, B. A. Krentsel and L. N. Andreev

Synthesis of alkyl-substituted chlorobenzenes is of theoretical interest from the point of view of the study of the influence of substituents on the alkylation of aromatic hydrocarbons, and it also has a practical significance in connection with the use of alkylchlorobenzenes for the preparation of certain kinds of synthetic rubber.

Data on the alkylation of chlorobenzene by halo derivatives of hydrocarbons in the presence of aluminum chloride are in the literature. Thus, the reaction of chlorobenzene with isoamyl chloride in the presence of $AlCl_3$ has been studied at 100° and a ratio of reagents and catalyst ($C_6H_5Cl$: $i\text{-}C_5H_{11}Cl$: $AlCl_3$) of 3.5: 0.5: 1 [1]. Under these conditions, p-chloro-tert-amylbenzene is formed.

Instead of an isoalkyl chloride, ethyl bromide was used as the alkylating agent in another investigation [2]. The product of the reaction at 100° was p-chloroethylbenzene. Cyclohexylchloride has been used for the preparation of p-chlorocyclohexylbenzene [3].

The alkylation of o-dichlorobenzene with methyl chloride in the presence of aluminum chloride at 100° and 12 hours contact time leads to the formation of trichloromesitylene and hexamethylbenzene [4].

In the work of Yu. G. Mamedaliev and Sh. Veliev [5] on the alkylation of chlorobenzene with propylene and butylene using a cracked gas fraction (22% $C_3H_6$, 77% $C_3H_8$, and ~1% $C_4$) as the alkylating agent, when the alkylation was carried out at a temperature of 350°, a pressure of 20 atm., and a space rate of 0.3, the yield of chloroisopropylbenzene is 84% of theoretical. A similar yield of chlorobutylbenzene is obtained by the alkylation of chlorobenzene with butylene at a temperature of 350° and a pressure of 40 atm.

In the progress of previous investigations on the alkylation of different classes of hydrocarbons with alkyl chlorides in the presence of $AlCl_3 \cdot HSO_4$ complex, we studied the reaction of chlorobenzene and isopropyl chloride in the presence of this catalyst.

## EXPERIMENTAL

For the reaction of chlorobenzene and isopropyl chloride

$$C_6H_5Cl + i\text{-}C_3H_7Cl \rightarrow i\text{-}C_3H_7[C_6H_4]Cl + HCl$$

we used commercial reagent grade chlorobenzene ($n_D^{20}$ 1.5248, $d_4^{20}$ 1.1099; for chemically pure benzene, $n_D^{20}$ 1.5246, $d_4^{20}$ 1.1054). The isopropyl chloride was prepared by the usual method – by the reaction of isopropyl alcohol with concentrated hydrochloric acid in the presence of zinc chloride.

The reaction of chlorobenzene with isopropyl chloride was carried out in a three-necked flask fitted with a stirrer and reflux condenser. A known amount of chlorobenzene and the catalyst were charged to the reaction flask, and then, with stirring, the calculated amount of isopropyl chloride was gradually added.

TABLE 1

| | Fraction | | | | |
|---|---|---|---|---|---|
| | I | II | III | IV | V |
| $n_D^{20}$ | 1.3990 | 1.5131 | – | 1.5160 | 1.5118 |
| $d_4^{20}$ | 0.8858 | 1.0820 | 1.0840 | 1.0872 | 0.99 |
| Mol. wt. | 82.7 | 113 | 122 | 148.6 | 183.8 |

After addition of the chloride was complete, the reaction was held for a time at a temperature of 30-35°. At the conclusion of the reaction, the flask containing the reaction mixture was cooled with ice water, and the contents were treated with water to decompose the catalyst.

The hydrocarbon layer was separated, washed with water, neutralized with a 10-15% solution of soda, and dried over calcined calcium chloride.

**TABLE 2**

Composite Table of Experiments on the Alkylation of Chlorobenzene with Isopropyl Chloride[1]

| Expt. No. | Chloro-benzene ml | Isopropyl chloride, ml | Mole ratio | Catalyst g/mole | Yield, in % of theory, of the fractions | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | > 145° | 145-170° | 170-210° | 210-240° | > 240° |
| 1[4] | 101.5 | — | — | 10 | — | — | — | — | — |
| 2 | 101.5 | 91.5 | 1 : 1 | 10 | 74.7 | 16.2 | 40.7 | 16.5 | 1.3 |
| 3 | 101.5 | 91.5 | 1 : 1 | 5 | 55.9 | 20.4 | 16.8 | 16.2 | 2.5 |
| 4 | 101.5 | 91.5 | 1 : 1 | 2.5 | 22.0 | 11.0 | 3.9 | 5.7 | 1.4 |
| 5 | 101.5 | 91.5 | 1 : 1 | 10 | 80.5 | 17.8 | 48.7 | 22.7 | 1.3 |
| 6 | 101.5 | 91.5 | 1 : 1 | 7.5 | 77.0 | 24.2 | 21.0 | 28.8 | 3.0 |
| 7 | 101.5 | 91.5 | 1 : 1 | 12.5 | 82.4 | 11.1 | 48.5 | 21.8 | 1.0 |
| 8 | 101.5 | 91.5 | 1 : 1 | 10 | 92.7 | 21.4 | 32.8 | 36.2 | 2.3 |
| 9[2] | 101.5 | 91.5 | 1 : 1 | 10 | 81.6 | 20.4 | 37.4 | 22.4 | 1.4 |
| 10[3] | 101.5 | 91.5 | 1 : 1 | 12.5 | 72.0 | 12.3 | 30.1 | 19.5 | 1.1 |
| 11[4] | 101.5 | 91.5 | 1 : 1 | 10 | 86.2 | 14.5 | 53.0 | 17.2 | 1.5 |
| 12 | 101.5 | 91.5 | 1 : 1 | 12.5 | 63.0 | 6.8 | 38.8 | 15.1 | 2.3 |
| 13 | 101.5 | 47 | 1 : 0.5 | 12.5 | 62.8 | 2.0 | 38.8 | 13.2 | 5.8 |
| 14[2] | 101.5 | 91.5 | 1 : 1 | 12.5 | 22.4 | — | 7.2 | 9.1 | 6.1 |
| 15 | 101.5 | 47 | 1 : 0.5 | 12.5 | 62.0 | 3.5 | 28.2 | 17.0 | 5.3 |
| 16 | 206 | 137 | 2 : 0.5 | 25.0 | 37.1 | 1.4 | 18.7 | 12.4 | 2.8 |
| 17[3] | 101.5 | 91.5 | 1 : 1 | 12.5 | 16.5 | 1.1 | 5.5 | 5.6 | 4.3 |
| 18 | 101.5 | 91.5 | 1 : 1 | 12.5 | 33.8 | 1.7 | 16.5 | 12.2 | 3.4 |
| 19[3] | 102 | (82 + 10) | 1 : 1 | 12.5 | 32.4 | 1.2 | 12.4 | 12.5 | 6.3 |
| 20[3] | 102 | 91.5 | 1 : 1 | 12.5 | 19.4 | 0.7 | 8.1 | 8.0 | 2.6 |
| 21[3] | 102 | (85 + 6) | 1 : 1 | 12.5 | 40.7 | 2.0 | 22.8 | 13.3 | 2.8 |
| 22 | 102 | 91.5 | 1 : 1 | 12.5 | 76.3 | 5.4 | 46.0 | 21.9 | 3.0 |
| 23 | 102 | (68.0 + 23.5) | 1 : 1 | 12.5 | 24.5 | 8.1 | 45.7 | 14.7 | 6.8 |
| 24 | 102 | 91 | 1 : 1 | 12.5 | 81.9 | 9.4 | 50.0 | 14.2 | 8.9 |
| 25 | 205 | 46 | 2 : 0.5 | 12.5 | 78.7 | 8.8 | 64.2 | 5.7 | — |
| 26 | 205 | 46 | 2 : 0.5 | 12.5 | 72.8 | 8.1 | 67.2 | 4.5 | |
| 27 | 102.5 | 92 | 1 : 1 | 25.0 | 67.8 | 1.8 | 45.0 | 16.5 | 4.7 |
| 28 | 102.5 | 92 | 1 : 1 | 25.0 | 64.9 | 2.9 | 40.0 | 16.8 | 5.2 |
| 29 | 102.5 | 92 | 1 : 1 | 25.0 | 68.0 | 2.9 | 45.0 | 15.1 | 4.9 |
| 30 | 102.5 | 92 | 1 : 1 | 10.0 | 73.0 | — | — | — | — |
| 31 | 102.5 | 92 | 1 : 1 | 10.0 | 74.4 | — | — | — | — |
| 32 | 102.5 | 92 | 1 : 1 | 10.0 | 71.2 | — | — | — | — |
| 33 | 102.5 | 92 | 1 : 1 | 10.0 | 65.3 | — | — | — | — |
| 34 | 102.5 | 92 | 1 : 1 | 10.0 | 71.8 | — | — | — | — |
| 35 | 102.5 | 92 | 1 : 1 | 10.0 | 66.0 | — | — | — | — |
| 36 | 102.5 | 92 | 1 : 1 | 10.1 | 73.2 | — | — | — | — |
| 37 | 102.5 | 92 | 1 : 1 | 10.0 | 74.4 | — | — | — | — |
| 38 | 102.5 | 92 | 1 : 1 | 10.0 | 74.4 | — | — | — | — |

[1]. The yields in all columns of the table were calculated on chloroisopropylbenzene.
[2] Old catalyst. [3]. Time, 45 minutes. [4]. The reagents have already been in a reaction.

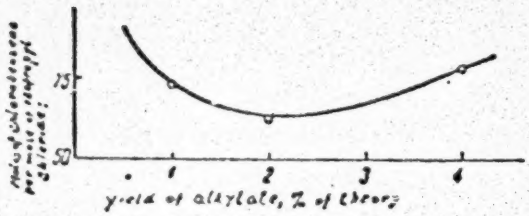


Fig. 1. Alkylation of chlorobenzene with isopropyl chloride. Effect of reagent ratio.

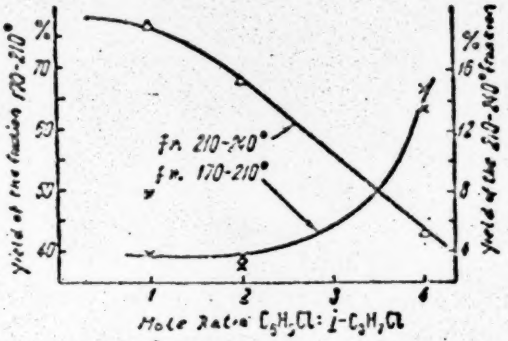


Fig. 2. Alkylation of chlorobenzene with isopropyl chloride. Effect of mole ratio on the yields of different fractions.

The dry alkylate was distilled into the following fractions: Fraction I, 90-100°; Fraction II, 100-145°; alkylate; Fraction III, 145-170° – intermediate fraction; Fraction IV, 170-210° (more than 80% of the fraction boiled in the range 192-197°) – chloroisopropylbenzene fraction; Fraction V, 210-240° – polyalkylchlorobenzenes.

The physicochemical properties of the fractions are presented in Table 1.

Inspection of the data of Table 2 shows that the yield of alkylate (in experiments carried out under the same

conditions, see Experiments 30-38) ranged from 65 to 74% with an average of 71.5% of theoretical.

The effect of reagent ratio on the total yield of alkylate is shown graphically in Figure 1, from which it is seen that a change in the ratio i-$C_3H_7Cl$: $C_6H_5Cl$ within the limits of 1:1 to 1:4 has little effect on the total yield of alkylation products. However, as shown graphically in Figure 2, an increase in the excess of chlorobenzene in the original reaction mixture leads to a decrease in the amount of polyalkyl derivatives formed and to a corresponding increase in the yield of the chloroisopropylbenzene fraction.

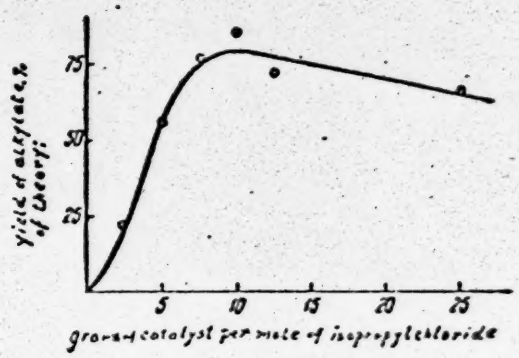


Fig. 3. Alkylation of chlorobenzene with isopropyl chloride. Effect of amount of catalyst, $AlCl_3 \cdot HSO_4$.

In Figure 3 is shown the effect of amount of catalyst on the total yield of alkylate (experiments 2-10, 17, 18, 27, 28 and 29). As follows from the graph, the yield of alkylate depends on the amount of catalyst, and it is characterized by a maximum which was found by us earlier during a study of the alkylation of aromatic hydrocarbons with alkyl chlorides in the presence of $AlCl_3 \cdot HSO_4$.

With the aim of accumulating alkylate, 9 experiments were carried out under identical conditions (a mole ratio of chlorobenzene to isopropyl chloride of 1:1, 10 grams of catalyst per mole of isopropyl chloride, a reaction time of 3 hours).

Properties of the chloroisopropylbenzene fraction of the alkylate (170-210°) are presented in Table 3.

TABLE 3

| | 192-197° fraction (about 85% of the 170-210° fraction). | Literature data for p-chloroisopropylbenzene | 208-210° fraction (chlorodiisopropylbenzene |
|---|---|---|---|
| $d_4^{20}$ | 1.0268 | 1.0257 | 1.0077 |
| $n_D^{20}$ | 1.5138 | 1.5140 | 1.5125 |
| Mol. wt. | 157.6 | 154.5 | 220 |
| Br No. | 1.3 | — | 1.7 |
| Cl content, % | 22.2 | 22.9 | — |

Oxidation of the 192-197° fraction with $KMnO_4$ gave p-chlorobenzoic acid. Consequently, alkylation of chlorobenzene with isopropyl chloride in the presence of $AlCl_3 \cdot HSO_4$ yields primarily p-chloroisopropylbenzene.

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Received October 19, 1955

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# EXCHANGE OF SULFATE IONS IN SOLUTIONS OF BASIC CHROMIUM SULFATE

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(Presented by Academician L. L. Chernyaev, September 9, 1955)

Upon the addition to a solution of violet chromium sulfate of approximately 0.14 g-equiv. of an alkali per g-equiv. of chromium suspension appears. In time, the suspension dissolves. The solution turns green. According to E. Stiasni [1], the suspension consists of difficulty soluble dihydroxytetraaquochromium sulfate formula, $[Cr(OH)_2(OH_2)_4]_2SO_4$. Stiasni explains the solution of the suspension by a process of olation. The addition of alkali to a solution of chromium sulfate which had first stood for a long time did not cause the formation of a soluble suspension, owing to the ol-compound which had already formed during aging of the solution. The formation of a precipitate which did not dissolve with the passage of time (probably chromic hydroxide) occurred only upon the addition of approximately 0.6 g-equiv. of alkali per g-equiv. of chromium.

It cannot be considered that the composition and structure of basic chromium sulfate complexes in solution have been explained. The presence of complexes containing from 1 $OH^-$ per 2 $Cr^{3+}$ to 2 $OH^-$ per 1 $Cr^{3+}$ is assumed. These complexes contain $SO_4^{2-}$ ions in the inner coordination sphere of the chromium. Moreover, they are, in some degree, associated.

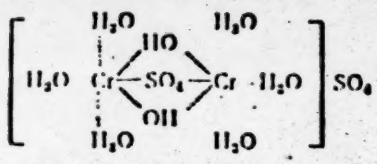
Some authors [2, 3] assume the existence of individual complex salts in solutions into which 0.33 g-equiv. of alkali per g-equiv. of chromium has been introduced.

During a study of chromium sulfate complexes by ion exchange, Gustavson [4] came to the conclusion that such complex ions contain 1 sulfate group per 2 atoms of chromium; therefore, there are two types of bonds for the sulfate groups. The more stably bonded sulfate group forms a bridge between two atoms of chromium, and the less stably bonded sulfate group is bonded to only one chromium.

Gustavson [4] ascribed to the complex ion the structure

$$\left[\begin{matrix} Cr-O-Cr-SO_4-Cr-O-Cr \\ | \qquad\qquad\qquad\qquad\qquad | \\ SO_4/2 \qquad\qquad\qquad\qquad SO_4/2 \end{matrix}\right]^{4+}$$

I. P. Stakhov [2] considers that this complex has the structure



However, Erdmann [5] ascribed such a structure to the complex formed by boiling a dilute solution of green chromium sulfate (without the addition of alkali).

We have assumed that the study of the exchange of $SO_4^{--}$ ions between the outer and inner coordination spheres of chromium sulfate complexes in solutions of basic chromium sulfate helps to explain their structure. The possibility of studying the process of $SO_4^{--}$ exchange by means of tagged sulfur has been demonstrated with solutions of green chromium sulfate of neutral basicity (prepared without the addition of alkali) [6].

Chromium sulfate was prepared from chromium trioxide by reduction with sulfur dioxide. The thoroughly boiled solution was allowed to stand for two weeks. The basic chromium sulfate was prepared by adding barium hydroxide to the solution. The solution of basic chromium sulfate was allowed to stand for a week, and was then analyzed.

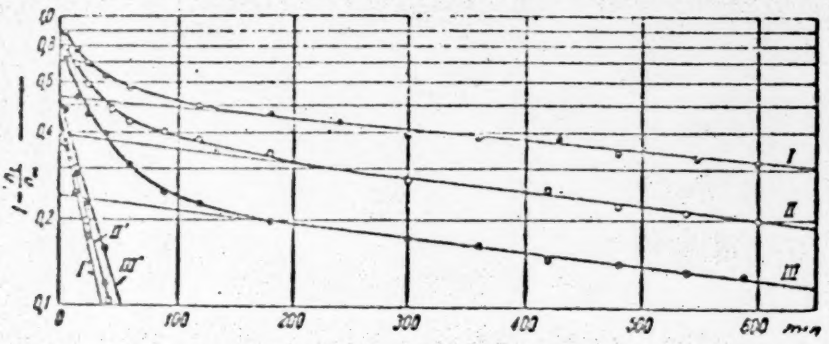



Fig. 1. Curves of $SO_4^{--}$ exchange between the outer and inner coordination spheres of chromium. Experimental curves: I) for chromium sulfate solutions in which 20% of the $SO_4^{--}$ was substituted by hydroxyl groups (20% basicity); II) 40%; III) 53%. Calculated for the faster process: I') from Curve I; II') from Curve II; III') from Curve III.

The exchange process was carried out in a thermostat at 20 ± 0.05°. A certain amount of $Na_2SO_4$ containing a radioactive isotope of sulfur $S^{35}$, was introduced into the solution. The amount of $Na_2SO_4$ was insignificant in comparison with the amount of chromium sulfate. The solution was allowed to stand in the thermostat for a given length of time, after which the sulfate ions of the outer and inner coordination spheres could be quickly separated. The separation was carried out by means of benzidine hydrochloride, which precipitated immediately only the $SO_4^{--}$ of the outer sphere. The precipitate of benzidine sulfate was filtered off, and the $SO_4^{--}$ of the inner coordination sphere was precipitated from the filtrate in the form of barium sulfate.

The barium sulfate precipitate was filtered off, and prepared for the activity determination. The samples were placed in a fixed position relative to the end window counter, and their activities were measured. The necessary corrections were introduced into the experimentally determined activities.

The results of the measurements on a solution 0.79 N with respect to chromium are presented in Figure 1. Time is plotted on the abscissa, and the logarithm of $(1-nt/n_\infty)$ (where $nt$ is the activity of the sample taken at time $t$; $n_\infty$ is the activity of the sample taken after the end of the exchange process) is plotted along the

ordinate. As seen from the Fig. 1, the points fall on the curves which, with an increase in time, become a straight line. That, when plotted semilogarithmically, the points fall not on a straight line, but on a curve indicates the presence in the system of some different exchange processes which proceed at different rates. The cause of this could be the unequal bonds of the $SO_4^{--}$ ions in the inner coordination sphere of the chromium complex or the presence of different complexes in the solution.

Instances of such complex curves for exchange reactions have not been published [7]. An exception is a curve for an exchange process in a system where a part of the atoms exchanged at a measurable rate and the other part were practically unexchanged. Such a curve can be converted relatively easily into a straight line representing only the process which proceeds with a measurable rate.

It is rather easy to treat the results of measurements of the kinetics of complex reactions of isotope exchange under conditions where the concentration of the material into which the tagged atoms were introduced is much greater than that of the material with which the exchange is carried out. The concentration must be so great that the isotope composition of the original tagged material remains practically constant. In this case, the exchange processes proceed independently of one another, and the curves can be separated into straight lines corresponding to separate exchange processes of identical, equally bonded atoms. This separation is carried out analogously to the separation into straight lines of complex curves for the decomposition of mixtures of independently decomposing radioactive isotopes [7]. For the remaining cases of isotope exchange, which occur in complex systems, the exchange rate for each of the processes is a function of the exchange rates of the other processes, and, therefore, treatment of the results is more complex.

We carried out the treatment of the exchange curves considering the processes to be independent. This certainly introduced an error into the results obtained; however, as a result of the rather considerable difference in the rates of exchange of each of the processes, the error could not be great. It is quite probable that it was less than the error in the measurements.

The curves obtained, presented in Figure 1, are rather well separated into two straight lines. The period of half-life for each of the processes was determined from the lines. For the evaluation of the accuracy of the values obtained, we determined a correction, with the aid of which the experimental results were extrapolated to zero exchange at t = 0. After introducing the correction, we calculated the half-life period for each of the separate measurements. The error did not exceed $\pm$ 10%.

It was shown that the exchange reaction proceeded according to the first order law, and was independent of the amount of alkali added to the solution of chromium sulfate (independent of basicity). The half-life period for the fast reaction for the solution 0.79 N with respect to chromium, into which was introduced 0.2 g-equiv. of alkali per g-equiv. of chromium, was 22 minutes; for the solution with 0.4 g-equiv. of alkali it was 23 minutes; for the solution with 0.53 g-equiv. of alkali it was 20 minutes. The half-life periods for the slower processes were, respectively, 830 590 and 610 minutes.

The results obtained show that in solutions of basic chromium sulfate containing from 0.2 to 0.53 g-equiv. of alkali per g-equiv. of chromium there are only two types of bonds for $SO_4^{--}$ ions in the inner coordination sphere of the chromium. With an increase in the amount of added alkali there was an increase in the amount of faster exchanging sulfate ions and a decrease in the amount of slower exchanging ions. The exchange rate remained first order. In connection with this, the assumption seems probable that with the introduction of 0.33 g-equiv. of alkali per g-equiv. of chromium into the solution under the conditions of the experiment, there was not formed, in any case, a new definite complex, which was stable and which was present in significant quantity.

In such a case, the difference in the rates of exchange of the ions, just as in the phenomenon observed by Gustavson [4] during an ion-exchange study, are dependent, not on the inequality of the bonds in one complex molecule, but on the presence of two different complexes. These chromium sulfate complexes differ in the number of hydroxyl groups in the inner coordination sphere. The introduction of a hydroxyl group into the inner sphere of the chromium causes the formation of olified polynuclear chromium complexes. The addition of $SO_4^{--}$ ions to such complexes is probably dependent on an increase in the overall electrostatic field of such complex ions, which are complicated in comparison with the simple chromium ion, and is also dependent on the greater steric efficiency of the addition of $SO_4^{--}$ ion simultaneously to two chromium ions with hydroxyls bonded between them. Our experimental data show that a further increase in the number of hydroxyls bonded to the chromium ion causes some labilization of the bond on the chromium with $SO_4^{--}$ ions. It is possible that this phenomenon is explained by an electrostatic repulsion of the identically charged ions or by the greater trans effect of the hydroxyl ions in comparison with water molecules [8]. The latter can be proved only by a detailed study of the structure of basic chromium sulfate complexes.

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Received May 16, 1955



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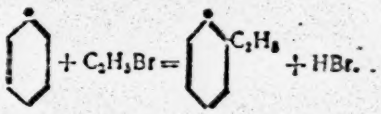
# SYNTHESIS OF 2-ETHYLANTHRAQUINONE TAGGED WITH CARBON $C^{14}$ IN THE NUCLEUS

Associate Member of the Academy of Science USSR A. P. Terentyev, S. V. Syavtsillo, V. I. Savushkina, E. M. Zhernovskaya and B. A. Charskaya

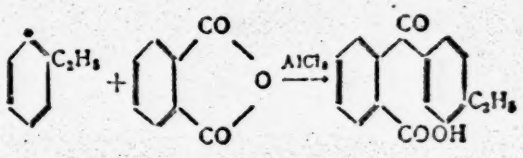
A series of methods is described in the literature [1-3] for the preparation of anthraquinone and certain of its derivatives with $C^{14}$ in the 9 position. For our purposes, it was necessary to develop a method for the preparation of ethylanthraquinone tagged with $C^{14}$, containing an ethyl group.

2-Ethylanthraquinone tagged with carbon $C^{14}$ was prepared by the following method:

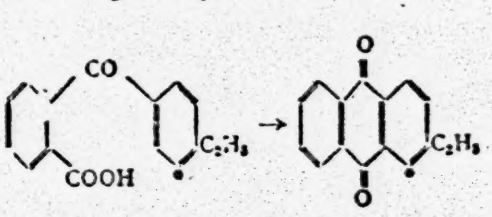
1. Ethylation of benzene with ethyl bromide in the presence of aluminum chloride:



2. Condensation of the ethylbenzene with phthalic anhydride in the presence of aluminum chloride:



3. Closing of the anthraquinone ring in the presence of oleum:



The synthesis of benzene tagged with carbon $C^{14}$ has been described previously in articles by Fields and Leaffer [4] and by Turner and Warne [5] and also in our previous communication [6]*.

In the preparation of the ethylbenzene, in order to obtain more complete utilization of the tagged benzene, we used an equivalent ratio of benzene to ethyl bromide, in distinction to the published methods in which an excess of benzene with respect to ethyl bromide is used.

* In a communication by V. I. Savushkina, S. V. Syavtsillo and A. P. Terentyev, through an oversight, the authors failed to cite the previous work of the American authors cited in this communication.

Synthesis of ethylbenzene *. Synthesis of the ethylbenzene was carried out in the apparatus shown in Figure 1. The round-bottomed flask, 1, was joined to a sleeve and mercury seal with stirrer, 2; the flask was also fitted with a reflux condenser, 3, which was joined through a calcium chloride tube to a wash bottle, 4, containing water. The slightly bent tube, 5, was barely submerged in the liquid contained in flask 1.

Into the mixture in flask 1, consisting of 20 g (0.256 mole) of benzene and 6.1 g (0.046 mole) of sublimed aluminum chloride (GOST** 4452-48), was passed dry hydrogen chloride over a period of 45 minutes.

Slightly bent tube, 5, was then exchanged for a dropping funnel from which was added freshly distilled ethyl bromide (28 g, 0.256 mole) while cooling the reaction flask with ice. The contents of the flask were then heated to 100° with constant stirring. After resolution of the reaction mixture with water, the separated upper layer, a mixture of benzene, ethylbenzene and polyalkylbenzenes, was neutralized with a 1 % solution of soda, washed with water, dried with fused calcium chloride, and distilled in a fractionating column.

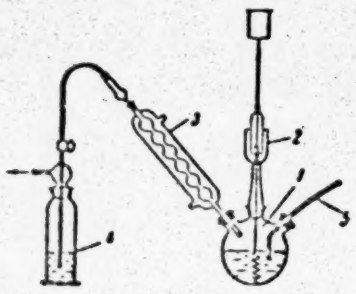


Fig. 1.

The resulting ethylbenzene had the following constants: b.p., 133-137°; $d_4^{20}$ 0.8650; $n_D^{20}$ 1.4953. Literature data: b.p., 136°; $d_4^{20}$ 0.867; $n_D^{20}$ 1.4953.

Synthesis of 4'-ethyl-2-benzoylbenzoic acid. The reaction was carried out in a round-bottomed flask provided with a mechanical stirrer, a thermometer, and a reflux condenser. To a mixture of ethylbenzene (7.5 g, 0.071 mole) and chlorobenzene (66.5 g, 0.59 mole) was gradually added pure (GOST 10914-40), powdered phthalic anhydride (10 g, 0.067 mole). Aluminum chloride (28 g, 0.21 mole) was added to the suspension with a gradual increase in temperature to 35-40°, and the reaction mixture was held for an hour at 35-40°.

TABLE 1

Radioactivity and Yield, on a Radioactivity Basis, of Ethylbenzene

| Expt. No. | Ethylbenzene obtained, (g) | Total radioactivity of the ethylbenzene (μc) | Yield on a radioactivity basis, % of original ethylbenzene |
|---|---|---|---|
| 1 | 8.5 | 142 | 29 |
| 2 | 5.0 | 320 | 25 |
| 3 | 10.8 | 1110 | 30 |

TABLE 2

Radioactivity and Yield, on a Radioactivity Basis of 4'-Ethyl-2-benzoylbenzoic acid

| Expt. No. | 4'-Ethyl-2-benzoylbenzoic acid obtained (g) | Total radioactivity basis, % of the 4'ethyl-2-benzoylbenzoic acid (μc) | Yield, on a radioactivity basis, % of original ethylbenzene |
|---|---|---|---|
| 1 | 10.2 | 270 | 84 |
| 2 | 20.2 | 910 | 82 |

10% sulfuric acid (80 ml) was put into another round-bottomed flask provided with a dropping funnel, a thermometer, and a reflux condenser, and heated to 55°. The reaction mass prepared above was added with stirring to the sulfuric acid at a rate such that the temperature in the flask did not rise above 95°.

Chlorobenzene was steam distilled from the separated upper layer. From the heated material in the distillation flask was separated a lower oily layer to which was added 50 ml of water and a 10% solution of soda until a stable alkaline reaction with brilliant yellow indicator was obtained.

The solution was filtered, and 4'-ethyl-2-benzoylbenzoic acid was separated from it by neutralization with an excess of 10% sulfuric acid; the 4'-ethyl-2-benzoylbenzoic acid was washed with water until a neutral reaction was obtained and dried at 100°. M.p. 124-126°; literature data, m.p. 127°.

* The method for the synthesis of ethylbenzene was worked out by R. M. Pozinskaya using non-radioactive materials.

** All-Union State Standard

TABLE 3

Radioactivity and Yield, on a Radioactivity Basis, of 2-Ethyl-anthraquinone

| Expt. No. | 2-Ethylanthraquinone obtained, (g) | Total radioactivity of the 2-ethylanthraquinone, (μ c) | Yield, on a radioactivity basis% of original ethylbenzene |
|---|---|---|---|
| 1 | 11.0 | 59 | 55 |
| 2 | 6.2 | 190 | 58 |
| 3 | 14.6 | 820 | 75 |

Condensation of 4'-ethyl-2-benzoylbenzoic acid to 2-ethylanthraquinone. Into a round bottomed flask fitted with a mechanical stirrer, a thermometer, and a reflux condenser was charged 160 g of 8% oleum. The latter was heated to 85°, and the 4'-ethyl-2-benzoylbenzoic acid was added to it portion-wise. The reaction mixture was maintained at 85-87° for 4 hours. The reaction mixture was cooled to room temperature and poured into ice water, the temperature rising to 90-95°. After cooling to 60°, the 2-ethylanthraquinone was filtered off, washed with warm water to the disappearance of the acid reaction, and fused at 125-130°. The ground 2-ethylanthraquinone was purified by sublimation at 80° and a pressure of 5 mm Hg. M.p. of the 2-ethylanthraquinone was 106-107°; literature value, m.p. 108°.

The yield of 2-ethylanthraquinone based on the original benzene was 15-22%.

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Received September 14,1955

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# DEHYDROCHLORINATION OF 1,1,1,3-TETRACHLORO-3-METHYLBUTANE

Academician A. V. Topchiev, N. F. Bogomolova and Yu. Ya. Goldfarb

The addition of carbon tetrachloride, chloroform, and other halo derivatives of methane to olefins by a radical mechanism with the formation of tri- and tetrahalo derivatives of the hydrocarbons has been described rather in detail in recent years [1]. There have been particularly detailed investigations of the properties and chemical transformations of 1,1,1,ω-tetrachloro derivatives prepared by the addition of carbon tetrachloride to ethylene [2]. It has been found that the ω-chlorine reacts with nucleophilic reagents such as $NH_3$, KCN, KI, sodiomalonic ester, etc., that the trichloromethyl group does not react with nucleophilic reagents but only with electrophilic reagents such as $AlCl_3$ and $FeCl_3$, and that the impossibility of hydrolyzing the trichloromethyl group in weakly acid, neutral, or alkaline media is connected with the inertness of this group [3]. Hydrolysis of the trichloromethyl group does occur under the influence of concentrated sulfuric acid in a strongly acid medium, and, as a result of the hydrolysis, ω-chloro carboxylic acids are obtained. By dehydrochlorination with alcoholic solutions of KOH it is possible to split out both one chlorine from the trichloromethyl group with the formation of $CCl_2 = CH(CH_2)_nCH_2Cl$, and also the ω-chlorine with the formation of $CCl_3(CH_2)_nCH = CH_2$ [4].

We investigated the addition of carbon tetrachloride to isobutylene in the presence of benzoyl peroxide at temperatures of 116-120°; the reaction was carried out in an autoclave. Under our conditions, the main product was that resulting from addition in a 1:1 ratio, that is, 1,1,1,3-tetrachloro-3-methylbutane (70-78% based on the isobutylene used), 64-65° (7 mm); $n_D^{20}$ 1.4550; $d_4^{20}$ 1.342; MR calculated 44.74, found 44.75.

Found %: C 28.65; H 3.90; Cl 67.40

$C_5H_8Cl_4$. Calculated %: C 28.57; H 3.81; Cl 67.62

In addition to the main product, there was obtained a small amount (3-5%) of the product obtained by the addition of $CCl_4$ to iso-$C_4H_8$ in a ratio of 1:2, $C_9H_{16}Cl_4$, b.p. 80-90° (1 mm), $n_D^{20}$ 1.4970.

Owing to the presence of the tertiary chlorine, the properties of the compound obtained differ somewhat from the properties of the straight chain compound obtained from the reaction of carbon tetrachloride with ethylene. For example, the reaction with aluminum chloride is more difficult.

1) 80 ml (108 g, 0.5 mole) of $C_5H_8Cl_4$, 88 ml (1.0 mole) of benzene, and 6 g of $AlCl_3$ were stirred at a temperature of −4 to −6° for 6.5 hours, and were again stirred for 11 hours at room temperature on the following day. Liberation of HCl was not noted. The reaction was black; on the bottom of the flask was a black residue from which a little yellow oil was liberated by decomposition of the residue with water. After distillation of the unreacted material, there remained several grams of a thick residue from which was isolated a fraction boiling at 80-113° (2 mm); 3.5 g; $n_D^{20}$ 1.5410; Cl content 21.56, 21.60%.

2) 80 ml $C_5H_8Cl_4$ in benzene solution was heated with 10 g of $AlCl_3$ at 90-97° for 4 hours in a flask fitted with a reflux condenser. Liberation of HCl was not observed. After distillation of the unreacted material, 1.5 g of a brown oil remained.

Dehydrochlorination proceeds readily in the presence of ferric chloride.

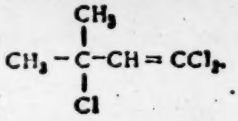
1) By heating 80 ml of $C_5H_8Cl_4$ dissolved in 90 ml of benzene with 1.0 g of $FeCl_3$ for 3.5 hours in a flask fitted with a reflux condenser and by simultaneously passing through the flask a slow stream of nitrogen, 20.35 g HCl, somewhat more than 0.5 mole, was collected in a solution of NaOH. After washing with a solution of soda and with water and distilling off the benzene, the residue was distilled under vacuum, and a fraction boiling at 32.5° (7 mm) was obtained; $n_D^{20}$ 1.4740.

Found %: C 34.46; 34.17; H 4.56; 4.54; Cl 61.24; 60.68

$C_5H_7Cl_3$. Calculated %: C 34.58; H 3.98; Cl 61.44

The material was very stable; on standing exposed to light and the atmosphere for a year, neither the color nor the empirical composition changed although it did decolorize bromine water. Evidently, in this case, as is

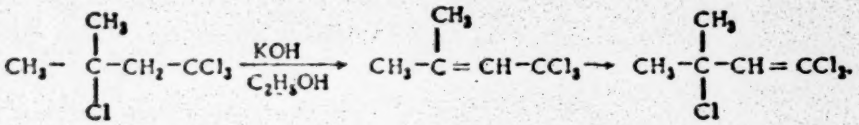
found In the case of straight chain compounds, chlorine was split from the trichloromethyl group to form



In addition to the main dehydrochlorination products, several grams of a material boiling in the range of 85-110° was obtained, $n_D^{20}$ 1.52–1.54; chlorine content 45%. The material was unstable; on standing, it rapidly turned yellow.

2) 80 ml of $C_5H_8Cl_4$, 405 ml of benzene, and 1.5 g $FeCl_3$ were heated in an autoclave at a temperature of 125-130° and a pressure of 1150 atm. for 3.5 hours. When the autoclave was opened the next day, a considerable amount HCl (not collected) was given off. After distillation of the benzene and unreacted $C_5H_8Cl_4$, there was obtained a heavy residue from which was liberated 10 g of material boiling at 70-124° (2-3 mm); $n_D^{20}$ 1.5340; Cl 37.25%. It can be assumed that this material was a product of the condensation of $C_5H_8Cl_4$ with benzene.

The dehydrochlorination of $C_5H_8Cl_4$ with an alcoholic solution of potassium hydroxide was carried out at 0°, room temperature, and somewhat above. Judging from the literature data [2], we could expect splitting off of the tertiary chlorine with a subsequent allylic rearrangement:



By using KOH in an amount somewhat over that required for splitting off 1 mole of HCl, we always obtained as the main reaction product an ether which was formed by the addition of the alcohol used as a solvent for the reaction (methyl, ethyl, n-propyl) to the double bond of the trichloroisopentene resulting from the dehydrochlorination. Methyl alcohol added more easily than ethyl, and ethyl added more easily than propyl. In the case of methyl alcohol, there was obtained an ether boiling at 43° (7 mm); $n_D^{20}$ 1.4670; $d_4^{20}$ 1.1624; MR calculated 40.81, found 40.34.

Found %: C 42.51; 42.57; H 6.22; 6.19; Cl 41.94; 41.99
$C_6H_{10}Cl_2O$. Calculated %: C 42.60; H 5.91; Cl 42.01

The ether obtained with ethyl alcohol boiled at 49° (7 mm); $n_D^{20}$ 1.4620; $d_4^{20}$ 1.1262; MR calculated 45.43; found 45.09.

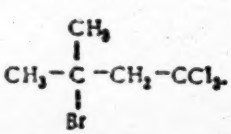
Found %: C 44.37; 44.23; H 6.39; 6.34; Cl 38.07
$C_7H_{12}Cl_2O$. Calculated %: C 45.90; H 6.55; Cl 38.80

These ethers were characterized by a pleasant odor; on standing, they turned yellow, splitting off HCl. The ethyl ether added to $BF_3$ forming a complex compound. It decolorized bromine water in the light. Quantitative addition of bromine did not occur, but the bromine addition product was isolated, and it boiled in the range 100-140°; $n_D^{20}$ 1.5790.

The addition of propyl alcohol proceeded with difficulty. The ether boiled at 60-64° (7 mm) (the boiling point corresponded to that of the original $C_5H_8Cl_4$); $n_D^{20}$ 1.4720. The product of the addition of phenol under these same conditions was obtained in small yield; the boiling range was very wide: 100-140° (7 mm); $n_D^{20}$ 1.5500.

In addition to the ethers, there was always obtained a small amount of material boiling in the range 20-25° (7 mm) (trap) with $n_D^{20}$ 1.5000. This material was very unstable, beginning to darken in the receiver of the vacuum column. On further standing, it completely resinified, liberating an upper layer of a colorless oil with $n_D^{20}$ 1.3900.

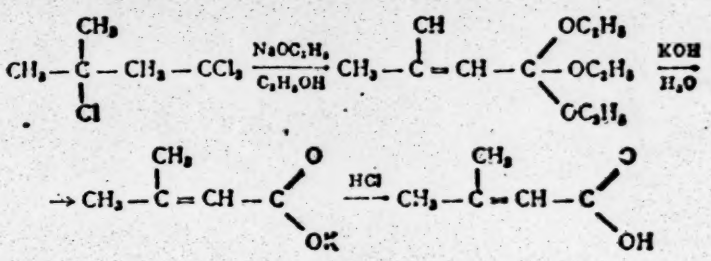
In an article by Kharasch and co-workers [5], in the description of the products of the addition of $CCl_3Br$ to various olefins, among others there was described the reaction of $CCl_3Br$ with isobutylene with the formation of



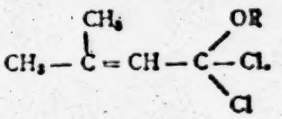
In this work, it was shown that β,β-dimethylacrylic acid is formed by the hydrolysis of the addition product with potassium alcoholate in an amount sufficient to split off all the atoms of halogen. We carried out this reaction

with our product, and β,β-dimethylacrylic acid in a yield of ~50% was obtained both with potassium alcoholate and with an alcoholic solution of KOH. This β,β-dimethylacrylic acid, after two recrystallizations from water, melted at 70° (handbook value, 69-70°). A mixture of the test sample with a known sample of β,β-dimethylacrylic acid also melted at 70°.

| | | |
|---|---|---|
| | Found %: | C 60.02; 60.11; H 8.08; 8.09 |
| $C_5H_8O_2$ | Calculated %: | C 60.00; H 8.00 |



This same acid was obtained by repeated treatment of the previously prepared methyl ether with an alcoholic solution of KOH. It can be assumed from this that the ether has the following formula:



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Received November 2, 1955



Institute of Petroleum
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* T p. = C.B. Translation pagination

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# SYNTHESIS OF SODIUM TRISILICATE IN THE CRYSTALLINE STATE AND A STUDY OF ITS PROPERTIES

Associate Member of the Academy of Science USSR P. P. Budnikov and M. A. Matveev

The system $Na_2O-SiO_2$ has been studied by many investigators. The most complete data are those of Kracek [1]; supplementary data on the equilibrium diagram of this system have been presented by Loeffler, by Morawitz and by Lillie [2-4]. There is no mention in these works of the formation of a compound corresponding in chemical composition to the formula $Na_2O \cdot 3SiO_2$; however, in commercial operations, alkali silicates corresponding to this composition are encountered in the vitreous state as the so-called silicate-block and silicate granulate

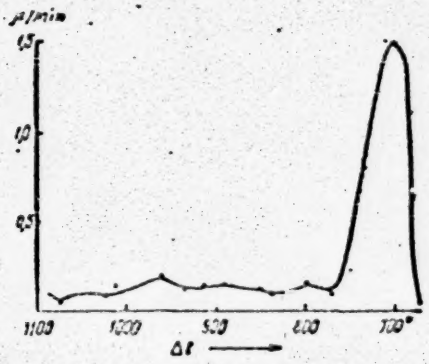


Fig. 1. Rate curve for the crystallization of $Na_2O \cdot 3SiO_2$.

Our investigations of the system $Na_2O-SiO_2$ have established that it is possible to form the compound $Na_2O \cdot 3SiO_2$ in the crystalline state, the compound having been synthesized from a homogeneous mixture of analytical grade, powdered, dehydrated silica and C.P. soda. The mixture of silica and soda, in a molar ratio $Na_2O : SiO_2 = 3 : 1$, was heated in a platinum crucible in an electric furnace to 1450°, and was maintained at this temperature for 2 hours. At the end of the soaking period, the silicate melt was cooled in the platinum crucible on a polished steel plate.

Chemical analysis of the glass obtained gave $SiO_2$ 75.35 % and $Na_2O$ 24.65%, which corresponds to the molecular formula $Na_2O \cdot 3SiO_2$. Crystallization of the vitreous sodium trisilicate was studied by the method of Ponomarev-Keshishyan [5,6]. Samples of this silicate were placed in a series of 2.5 mm diameter cells in a corundum specimen holder which was mounted on a porous, refractory block about 20 cm long, and the assembly was inserted into the Silit electric furnace. The temperature in the specimen holder, which was measured with Pt/PtRh thermocouples, was distributed over the range of 1100 to 600°. Soaking in this temperature interval was carried out for 4 and 6 hours, respectively.

The rate curve for the crystallization of vitreous sodium trisilicate is presented in Figure 1. From this curve it follows that the optimum temperature for the crystallization of vitreous $Na_2O \cdot 3SiO_2$ is 700°.

Thermal analysis of the vitreous and crystalline $Na_2O \cdot 3SiO_2$ resulted in the thermogram presented in Figure 2. The exothermic peak at 700° on the thermogram for vitreous $Na_2O \cdot 3SiO_2$ corresponds to its devitrification, and confirms the established optimum crystallization temperature of this compound. The endothermic effect at 750° corresponds to the fusion of crystalline $Na_2O \cdot 3SiO_2$; it is also observed on the thermogram for crystalline $Na_2O \cdot 3SiO_2$. The absence of an exothermic effect at 700° on the thermogram for crystalline $Na_2O \cdot 3SiO_2$ also confirms the crystallization of vitreous sodium trisilicate at this temperature.

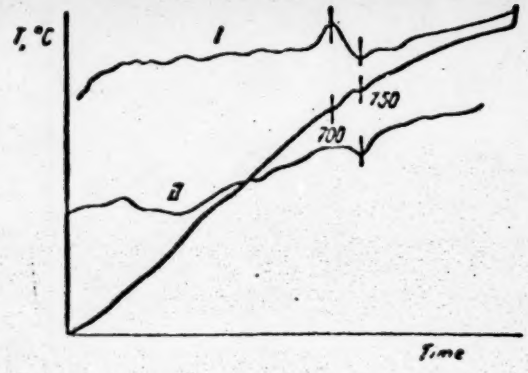


Fig. 2. Thermograms for vitreous (I) and crystalline (II) $Na_2O \cdot 3SiO_2$.

TABLE 1

| Intensity, I, of the interference lines according to the 10-point system | Interplanar distance, d, in kX | Intensity, I, of the interference lines according to the 10-point system | Interplanar distance, d, in kX |
|---|---|---|---|
| 1 | 5.550 | 3 | 2.010 |
| 1 | 5.075 | 3 | 1.948 |
| 5 | 4.100 | 2 | 1.879 |
| 3 | 3.840 | 1 | 1.747 |
| 4 | 3.686 | 1 | 1.640 |
| 4 | 3.491 | 1 | 1.610 |
| 2 b | 3.373 | 1 b | 1.536 |
| 3 | 3.149 | 2 | 1.464 |
| 3 b | 3.040 | 1 | 1.397 |
| 3 | 2.873 | 1 | 1.375 |
| 8 | 2.464 | 1 | 1.240 |
| 2 | 2.274 | 1 | 1.224 |
| 1 | 2.199 | 1 | 1.207 |
| 3 | 2.122 | 1 | 1.196 |
| 3 | 2.065 | 1 | 1.102 |

200 g of crystalline sodium trisilicate was synthesized by us for the study of its microstructure. Crystallization of this compound was carried out in the temperature interval 700-750° with alternate 3-hour soaking periods at the upper and lower limits of the temperature range for a total of 33 hours at 750° and 39 hours at 700°.

The investigation of the microstructure of crystalline sodium trisilicate under the polarizing microscope (sections prepared in kerosene) showed that the well-developed crystals differed in optical constants and syngony from the known crystalline mono- and disilicates of sodium [7], and represented a new form corresponding in composition to the formula $Na_2Si_3O_7$.

In the main, prismatic crystals were observed in the section. These crystals form well expressed spherulites (Figure 3), the length of the needles varying between 0.4 and 0.5 mm. The crystals are biaxial, optically negative with parallel and oblique extinction, and monoclinic syngony. The extinction angle varies within the limits of 20 to 40°. The refraction indices of the crystals were determined by the immersion method, and are: $N_g = 1.501-1.504$ (av. 1.5025); $N_p = 1.498-1.495$ (av. 1.4965). They exhibit double refraction $N_g - N_p = 1.5025 - 1.4965 = 0.006$. Finely ground (60μ) crystals of sodium trisilicate were studied by X-ray methods (iron anode, 12-hour exposures).

The results of the measurements of interplanar distances and the interference lines* are presented in Table 1. From the Table it is seen that, in the samples of $Na_2O \cdot 3SiO_2$ studied, lines for the interplanar distances of the crystalline mono- and disilicates of sodium are absent [7].

Determination of the density of $Na_2O \cdot 3SiO_2$ with three parallel samples by the pycnometer method using kerosene gave a value of 2.9443 for crystalline form and 2.5455 for the vitreous form. These figures show that the structure of vitreous sodium trisilicate is expanded in comparison with that of the crystalline form. The degree of expansion, determined from the ratio $[(2.9443 - 2.5455) \cdot 2.9443] \cdot 100$, is 13.5%. Dilatometric determinations of the linear thermal coefficient of expansion of sodium trisilicate in the vitreous and crystalline states were carried out in the temperature range 20-300°. The value at 300° for vitreous $Na_2O \cdot 3SiO_2$ is $108 \cdot 10^{-7}$, and for crystalline $Na_2O \cdot 3SiO_2$ it is $165 \cdot 10^{-7}$.

An important property of $Na_2O \cdot 3SiO_2$, which particularly characterizes its structures in the vitreous and crystalline states, is the rate at which these forms of the trisilicate go into solution. The rate of solution in water of crystalline and vitreous sodium trisilicate was determined by us by means of electrical conductivity at a temperature of of 20° on samples ground to an average particle diameter of 60μ. The results of the investigation are presented in Figure 4.

* Measurements carried out by Yu. P. Simanov.

Fig. 3. Crystals of $Na_2O \cdot 3SiO_2$ in polarized light ( 300X)

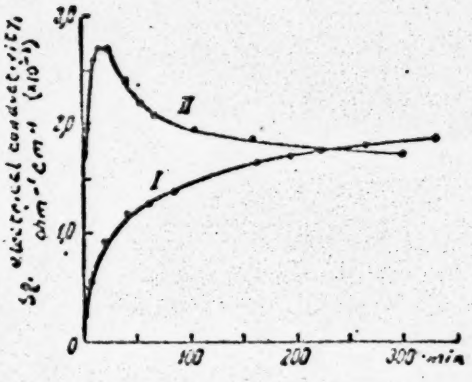


Fig. 4. Rate of solution of vitreous (I) and crystalline (II) sodium trisilicate in water.

The results of the investigation of solubility show that the electrical conductivity curve of crystalline $Na_2O \cdot 3SiO_2$ has a sharp maximum at a solution time of 15-20 minutes and $2.65 \cdot 10^{-3}$ $ohm^{-1}$. As this maximum is reached, there is observed in the solution the separation of a voluminous, white, flocculant precipitate, which is explained by the rapid hydrolysis of the crystalline $Na_2O \cdot 3SiO_2$ according to the equations

$$Na_2Si_3O_7 + 2H_2O \rightarrow H_2Si_3O_7 + 2Na^+ + 2(OH)^- \quad (1)$$

As a result, the precipitate contains the water-unstable silicic acid of the composition $H_2Si_3O_7$. Simultaneously, the concentration of sodium ions increases, and this causes a corresponding increase in the electrical conductivity of the solution giving rise to the maximum in the curve. The unstable silicic acid reacting with the water, forms, in all probability, water-unstable orthosilicic acid:

$$H_2Si_3O_7 + 5H_2O \rightarrow 3H_4SiO_4 \quad (2)$$

Orthosilicic acid dissociates in solution according to the equation $H_4SiO_4 \rightarrow 4H^+ + (SiO_4)^{4-}$. In connection with this, the hydrolytically formed $Na^+$ ions are linked in solution by $(SiO_4)^{4-}$ ions forming readily water-soluble sodium orthosilicates:

$$4Na^+ + (SiO_4)^{4-} \rightleftharpoons Na_4SiO_4 \quad (3)$$

This reaction will proceed until equilibrium is established between the $Na^+$ ions and the $(SiO_4)^{4-}$ ions. At the onset of this equilibrium, the concentration of free sodium ions in the solution substantially decreases, and the electrical conductivity gradually decreases and becomes constant.

The curve for the rate of solution of vitreous $Na_2O \cdot 3SiO_2$, Figure 4, shows a gradual increase in the electrical

conductivity of the silicate solution, whereupon during the solution of the vitreous $Na_2O \cdot 3SiO_2$, in distinction from the crystalline form, precipitation of a flocculant precipitate is not observed in the cited temperature and time intervals. The extent of hydrolysis occuring during solution of crystalline and vitreous $Na_2O \cdot 3SiO_2$ was determined by us from the amount of sodium hydroxide formed hydrolytically during the same time intervals. The results of this determination showed that, upon dissolution, crystalline $Na_2O \cdot 3SiO_2$ hydrolyzes strongly for the first 10 minutes (up to 70% of the total quantity). Such hydrolysis of crystalline $Na_2O \cdot 3SiO_2$ is, apparently, explained by the fact that in the crystalline state the sodium ions are disposed in a strictly determined and regular order, and because of this they are more available for the action of water on them simultaneously, so that the process of dissolution in the initial period proceeds more intensively and is characterized by a higher degree of hydrolysis. The structure of the vitreous form does not have such strict and regular recurrent distribution of sodium ions. On the contrary, it is expanded and little ordered with an uncentered distribution of sodium ions; because of this, the process of its passage into solution is accomplished more slowly and is not accompanied by vigorous hydrolytic decomposition; solution proceeds by diffusion, that is, the water gradually diffuses into the structure. As a result, there is a gradual leaching of the silicate and a slow accumulation of sodium ions in the solution, which is characterized by the smooth electrical conductivity curve for the solution of vitreous sodium trisilicate.

The investigation presented permits the following conclusions:

1. It was established that a new compound, $Na_2O \cdot 3SiO_2$, can be formed in the crystalline state in the system $Na_2O-SiO_2$ at a temperature of 700-750°.

2. Rate curves for the crystallization of vitreous $Na_2O \cdot 3SiO_2$ are given.

3. The microstructure was studied; the optical constants of the crystals and the interplanar distances of the lattice of crystalline sodium trisilicate were determined.

4. The tendency toward hydration of crystalline $Na_2O \cdot 3SiO_2$ was studied, and the density, solubility, and coefficient of thermal expansion were determined.

5. The study of the properties of crystalline $Na_2O \cdot 3SiO_2$ shows that the synthesis of high silica crystalline sodium silicates is possible by means of protracted crystallization of vitreous silicates of the same composition.

6. The investigation of the crystallization of vitreous $Na_2O \cdot 3SiO_2$ and thermal analysis of the vitreous and crystalline states show that the glasses of the system $Na_2O-SiO_2$, apparently, are constructed of the silicon-oxygen ions $SiO_3$, $Si_2O_5$, $Si_3O_7$, $Si_4O_9$, etc., as the basic structural elements of sodium silicates and which form chains of silicon-oxygen tetrahedrons in different combinations among themselves and the sodium ions. Upon prolonged soaking, at the optimum temperature, these structural elements form the crystalline structure of the silicates, passing over into their aggregate-stable-crystalline form.

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Received September 16, 1955



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# SYNTHESIS OF SOME ORGANOPHOSPHORUS COMPOUNDS AND AN INVESTIGATION OF THEIR EFFECTS ON THE PROPERTIES OF MINERAL OILS

P. I. Sanin and V. V. Sher

(Presented by Academician A. V. Topchiev, September 23, 1955)

In the present article are presented the results of the synthesis and investigation of a series of compounds, derivatives of dithiophosphoric and phosphoric acids, some representatives of which, as was established, are active complex additives of mineral lubricating oils. The investigation of the properties of the compounds synthesized presented the possibility of establishing rules connecting the structure of the compounds with their activity as additives. The value of the various organophosphorus compounds as additives for mineral lubricating oils can be appreciated just from the broad patent literature devoted to this question [1]; however, a systematic investigation in this field has not been carried out.

In accordance with the aim of the investigation, we synthesized: barium and nickel salts of esters of dithiophosphoric acid, containing hydrocarbon radicals of different structures (see Table 1, preparations 1-9) potassium dioctadecyldithiophosphate (No. 10), disulfides of the general formula $(RO)_2PSS-SSP(OR)_2$ (Nos. 11 and 12), and barium dioctadecyl phosphate (No. 13). The compounds synthesized are not described in the literature.

The esters of dithiophosphoric acid – dialkyl dithiophosphates – required for the preparation of the salts and sulfides were prepared by the reaction of phosphorus pentasulfide with alcohols [2-6]. Di-n-butyl dithiophosphate (b.p. 121.0-122.0° at 2.5 mm, $d_4^{20}$ 1.0689, $n_D^{20}$ 1.4940) and diisoamyl dithiophosphate (b.p. 147.0-148.0° at 2.5 mm, $d_4^{20}$ 1.0354, $n_D^{20}$ 1.4887), which were distilled under vacuum, were oily liquids; di-n-decyl- and di-(2-heptylundecyl) dithiophosphate, which were not distilled, were viscous liquids; di-n-octadecyl dithiophosphate was a white, amorphous material; di-n-octadecyl phosphate was a white crystalline material (m.p. 79.5-80.5°).

The barium salts were obtained by the reaction of barium hydroxide with the dialkyl dithiophosphates; the nickel salts were obtained by the reaction of the potassium dialkyl dithiophosphates with nickel sulphate. The disulfides were prepared by oxidation of the corresponding dithiophosphates with iodine in alkaline medium [6].

The barium dialkyl dithiophosphates were white, crystalline materials; the nickel salts were lilac-colored crystalline materials; the intensity of their color dying out with an increase in the molecular weight of the compound (of the hydrocarbon radicals).

1.5 % solutions of the synthesized materials in MS-20 mineral oil were investigated (Table 1); the effect of these materials on piston varnish was established using a PZV engine operating under standard conditions (maximum formation of piston varnish is represented by 5 points, no varnish by 0) and their effect on the corrosion of lead plates under standard conditions was also established. The mineral oil without additive gave a piston varnish of 4.5 points and a corrosion of 45.0 g/m².

From Table 1 it is seen that, in the series barium and nickel di-n-butyl-, diisoamyl-, di-n-decyl-, and di-n-octadecyl dithiophosphates, the activity of the compounds increases with an increase in the size of the hydrocarbon radicals. The most active, sharply reducing the formation of varnish and corrosion, were barium and nickel di-n-octadecyl dithiophosphates (preparations Nos. 4 and 9). The barium dioctadecyl dithiophosphate with branched radicals, namely, barium di-(2-heptylundecyl) dithiophosphate (preparation No. 5), was only a little less active than the compounds containing straight chain radicals (preparations Nos. 4 and 9). In addition, barium dithiophosphates with branched radicals are considerably more soluble in hydrocarbon media, and, therefore, are of considerably more interest as additives to mineral oil.

The disulfides synthesized (preparations Nos. 11 and 12) approximated the dithiophosphates in structure; the difference is that dithiophosphates of divalent metals contain the grouping –S–Me–S–, and in the disulphides the sulfur atoms are directly joined, –S–S–. From Table 1 it is seen that the disulfides have practically no inhibiting

TABLE 1

| Expt. No. | Preparation | Formula | M.p. (°C) | P (%) found | P (%) calc. | S (%) found | S (%) calc. | Ba or (%) found | Ba or (%) calc. | Test results • | Test results •• |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Barium di-n-butyldithiophosphate | $[(C_4H_9O)_2PSS]_2Ba$ | 136.0—138.0 | 10.02<br>9.97 | 9.99 | 20.05<br>20.31 | 20.69 | Ba 21.51<br>21.37 | 22.16 | 4.5 | 33.6 |
| 2 | Barium diisoamyldithiophosphate | $[(C_5H_{11}O)_2PSS]_2Ba$ | 179.0—180.0 | 8.70<br>8.71 | 9.16 | 19.10<br>19.13 | 18.97 | Ba 20.15<br>19.75 | 20.31 | 4.5 | 41.8 |
| 3 | Barium di-n-decyldithiophosphate | $[(C_{10}H_{21}O)_2PSS]_2Ba$ | — | 6.16<br>6.23 | 6.48 | 12.81<br>13.06 | 13.41 | Ba 13.19<br>13.47 | 14.36 | 1.5 | 0.9 |
| 4 | Barium di-n-octadecyldithiophosphate | $[(C_{18}H_{37}O)_2PSS]_2Ba$ | 99.0 100.0 | 4.09<br>4.11 | 4.41 | — | — | Ba 9.49<br>9.35 | 9.77 | 1.0 | 1.7 |
| 5 | Barium di-(2-heptylundecyl) dithiophosphate | $\left[\left(\begin{matrix}C_7H_{15}\\C_9H_{19}\end{matrix}\right)CHCH_2O\right)_2PSS\right]_2Ba$ | — | 4.15<br>4.13 | 4.41 | 8.83<br>8.90 | 9.12 | — | — | 1.5 | 5.1 |
| 6 | Nickel di-n-butyl dithiophosphate | $[(C_4H_9O)_2PSS]_2Ni$ | 16.0—16.5 | 11.25<br>11.16 | 11.46 | 23.39<br>23.35 | 23.69 | Ni 10.63<br>10.83 | 10.84 | 3.5 | 5.6 |
| 7 | Nickel diisoamyl dithiophosphate | $[(C_5H_{11}O)_2PSS]_2Ni$ | 23.5—24.5 | 10.42<br>10.27 | 10.37 | — | — | Ni 10.06<br>9.99 | 9.82 | 3.5 | 6.4 |
| 8 | Nickel di-n-decyl dithiophosphate | $[(C_{10}H_{21}O)_2PSS]_2Ni$ | 20.0—21.0 | 7.06<br>7.01 | 7.06 | 14.81<br>14.63 | 14.61 | Ni 6.67<br>6.64 | 6.68 | 1.5 | 11.0 |
| 9 | Nickel di-n-octadecyl dithiophosphate | $[(C_{18}H_{37}O)_2PSS]_2Ni$ | 50.5—51.5 | 4.59<br>4.66 | 4.67 | 9.33<br>9.18 | 9.67 | Ni 4.59<br>4.58 | 4.42 | 0.5 | 3.6 |
| 10 | Potassium di-n-octadecyl dithiophosphate | $(C_{18}H_{37}O)_2PSSK$ | 165.0—167.0 | 4.62<br>4.46 | 4.60 | 9.18<br>9.06 | 9.54 | — | — | 1.0 | 50.0 |
| 11 | Disulfide | $(C_4H_9O)_2PSS—SSP(OC_4H_9)_2$ | — | 12.74<br>12.65 | 12.84 | 26.37<br>26.57 | 26.80 | — | — | 5.0 | 97.1 |
| 12 | Disulfide | $(C_{18}H_{37}O)_2PSS—SSP(OC_{18}H_{37})_2$ | 39.0—40.0 | 4.68<br>4.59 | 4.89 | 10.08<br>9.84 | 10.12 | — | — | 4.0 | 4.3 |
| 13 | Barium di-n-octadecyl phosphate | $[(C_{18}H_{37}O)_2POO]_2Ba$ | ок. 200 | 4.57<br>4.54 | 4.62 | — | — | Ba 10.17<br>10.62 | 10,24 | 0.5 | 130.7 |

• Piston varnish points. [Note that this is a demerit system, not a merit system as is common in this country - Translator]

•• Corrosion in $g/m^2$.

effect on the formation of varnish; this latter property of additives, evidently, depends on the presence of metal atoms, for example, barium, nickel, or potassium, in compounds of the type of salts of dialkyl dithiophosphates (compare preparations Nos. 4, 9, 10, and 12). In addition, this property of additives is not connected with the presence of sulfur atoms in the dialkyl dithiophosphates, since barium di-n-octadecylphosphate (preparation No. 13) had the same activity as the corresponding dithiophosphate ester (preparation No. 4).

From the data presented, it follows that the chief carrier of anticorrosion properties in high molecular weight salts of dialkyl dithiophosphates is the sulfur (compare preparations Nos. 4, 9, and 13), and this is also confirmed by the results of the disulfide test (preparation No. 12).

An investigation of the dialkyl dithiophosphates as [pour point] depressors (additives increasing the fluidity of paraffin mineral oils at low temperatures) confirmed the previously developed ideas on the structure of depressors [7], and demonstrated the high activity of dialkyl dithiophosphates containing long hydrocarbon radicals of normal structure.

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Received September 20, 1955


* T.p. = C B. Translation pagination

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# SYNTHESES AND PROPERTIES OF SOME ALKYL ESTERS OF ETHANETHIOSULFONIC ACID

B. G. Boldyrev and A. K. Litkovets

(Presented by Academician I. N. Nazarov, September 26, 1955)

Alkyl esters (I) of alkanethiosulfonic acids are almost without description in the literature; nevertheless, they are of great interest, since in structure they suggest analogs (II) of the active principal of garlic [1] – the natural antibiotic allicin (III).

$Alk-SO_2-S-Alk'$ (I) $\quad Alk-SO-S-Alk$ (II)

$CH_2=CH-CH_2-SO-S-CH_2-CH=CH_2$ (III)

In the opinion of B. P. Tokin [2], the antibacterial properties of allicin and the lighter fractions separated from plants are related to a single group and represent the curative or protective powers of higher plants; in this case, it would be expected that allicin, its analogs (II), and the alkyl esters approaching it in composition (I) must possess high activity, especially against phytopathogenic bacteria.

For the further confirmation of this theory, the present work had for its goal the preparation of some alkyl esters (IV) of ethanethiosulfonic acid which, similarly to other compounds of the type of (I), are almost unknown up to the present:

$CH_3-CH_2-SO_2-S-Alk$ (IV) $\quad CH_3-CH_2-SO_2-SK$ (V)

The ethyl ester of ethanethiosulfonic acid has been prepared earlier by the oxidation of ethyl mercaptan [3] and by the reaction of potassium ethanethiosulfonate with ethyl bromide according to the reaction [4].

$$CH_3-CH_2-SO_2-SK + CH_3-CH_2-Br \longrightarrow CH_3-CH_2-SO_2-S-CH_2-CH_3 + KBr.$$

It was a heavy colorless or weakly yellow oil which distilled with decomposition at 130-140° and possessed a disagreeable, persistent odor of onions.

The ethanethiosulfonate required for this synthesis was prepared by the action of ethanesulfonyl chloride on an aqueous solution of potassium sulfide [4]:

$$CH_3-CH_2-SO_2Cl + K_2S \longrightarrow CH_3-CH_2-SO_2-SK + KCl.$$

The potassium ethanethiosulfonate was not isolated from the reaction mass; its alkaline solution was evaporated to dryness, was treated with boiling absolute alcohol, and the alcoholic solution was used directly for the preparation of the ethyl ester of ethanethiosulfonic acid by warming with ethyl bromide on a water bath.

The ethyl ester of ethanethiosulfonic acid has been more recently prepared by this same method [5], also without the isolation of the potassium ethanethiosulfonate. It had a b.p. of 56° at 0.2 mm; $n_D^{25}$ 1.4972.

At the same time, another method for its synthesis was described – the oxidation of diethyl disulfide with peracetic acid in ethyl acetate solution; the yield of final product by this method was only 12% of theoretical.

For the synthesis of the alkyl esters (IV), we made use of a well-known method [6, 7], the essence of which is expressed by the following series of equations:

$$CH_3-CH_2Br \xrightarrow{Na_2SO_3} CH_3-CH_2-SO_2Na \xrightarrow{PCl_5} CH_3-CH_2-SO_2Cl \xrightarrow{K_2S}$$
$$\longrightarrow CH_3-CH_2-SO_2-SK \xrightarrow{AlkBr} CH_3-CH_2-SO_2-S-Alk$$

We prepared potassium ethanethiosulfonate (V) by the reaction between ethanesulfonyl chloride and an aqueous solution of potassium sulfide with subsequent evaporation of the reaction mixture to dryness, extraction of the dry residue with butyl alcohol, and isolation of the crystalline product; after two-fold recrystallization from absolute alcohol, the potassium ethanethiosulfonate had a constant b.p. of 154°, and was a colorless crystalline material very readily soluble in water, readily soluble in boiling ethyl and butyl alcohols, and insoluble in ether, chloroform, and benzene.

It crystallizes from absolute alcohol in the form of thin plates, and from butyl alcohol in the form of flat needles.

Found %: S 39.10; 39.19

$C_2H_5O_2S_2K$. Calculated %: S 39.04

The alkyl esters (IV) of ethanethiosulfonic acid, the properties of which are presented in Table 1, were prepared by us by the reaction of potassium ethanethiosulfonate with alkyl halides in an aqueous acetone medium both at room temperature and with heating.

TABLE 1

Alkyl Esters of Ethanethiosulfonic Acid $CH_3-CH_2-SO_2-S-Alk$

| Alkyl group | B.p. in °C (1-2 mm) | $d_{20}^{20}$ | $n_D^{20}$ | $MR_D$ | | Sulfur, % | | Yield, % of theory |
|---|---|---|---|---|---|---|---|---|
| | | | | found | calc.* | found | calc. | |
| $CH_3-CH_2-$ | 102 | 1.1987 | 1.4985 | 37.75 | 37.90 | 41.65 | 41.58 | 78.0 |
| $CH_3-CH_2-CH_2$ | 109 | 1.1557 | 1.4954 | 42.48 | 42.52 | 38.02 | 38.11 | 70.0 |
| $CH_3$ \ CH– / $CH_3$ | 102-103 | 1.1489 | 1.4948 | 42.70 | 42.52 | 38.23 | 38.11 | 28.0 |
| $CH_2=CH-CH_2-$ | 109 | 1.1987 | 1.5161 | 41.90 | 42.05 | 38.54 | 38.57 | 86.0 |
| $CH_3-CH_2-CH_2-CH_2-$ | 116-117 | 1.1183 | 1.4916 | 47.26 | 47.14 | 35.32 | 35.18 | 55.0 |
| $CH_3$ \ $CH-CH_2-$ / $CH_3$ | 112-113 | 1.1327 | 1.4966 | 47.06 | 47.14 | 35.15 | 35.18 | 35.7 |

* The refractions of the group $>SO_2$ and of sulfide sulfur were taken as 8.63 and 8.00 (average values), respectively; exaltation of the group $-SO_2-S-$ was taken as + 0.6 [6,7].

At room temperature, the reaction proceeded very fast only with allyl bromide, being practically complete after 15-20 minutes; with ethyl, propyl, and butyl bromides the reaction proceeded considerably more slowly, reaching completion under these conditions only after several days; and, finally, with isopropyl and isobutyl bromides the reaction proceeded very poorly, and even after standing for 10 days the esters were obtained in yields of only 6-7 % of theory. Warming for two days on a water bath increased the yields of these esters to 28-30%. With the other alkyl halides used by us, upon warming on a water bath the reaction was complete in 3-4 hours giving yields of final products of 55-78% of theory.

This alkyl esters (IV) of ethanethiosulfonic acid, after vacuum distillation, were colorless, mobile, oily liquids with the sharp, persistent odor of onion or garlic, sometimes very disagreeable; they are very poorly soluble in water and very soluble in alcohol, ether, chloroform, acetone, benzene, and other organic solvents. They were completely unchanged after lengthy storage at room temperature, were stable to heating up to 120°, and were easily distilled under vacuum at a pressure of 1-2 mm Hg; however, they were partially converted to resins by this last treatment.

In physical properties they were very reminiscent of the alkyl esters of other alkanethiosulfonic acids [6, 7], and also of allicin (III) and its synthetic analog (II).

A study of the antibacterial activity of the esters (IV) synthesized by us, carried out at the D. K. Zabolotny

Institute of Microbiology of the Academy of Science USSR •, showed that the products (IV) exhibited bacteriostatic action on Staphyloc. aureus, B. coli, Mycobacter. $B_5$, and also on different fungi (mucor, Penicillium, Rhizopus, Aspergillus, Fusarium); hence, the activity of the esters (IV) depends to some extent on their structure and fluctuates within rather sharp limits.

The ethyl ester (VI) possessed the least activity with respect to Staphyloc. aureus. It is interesting that, according to the data of Verne and Small [5], this same ester was not inferior, and in a series of cases it preceded in bacteriostatic action on different forms of bacteria the analogous ester (VII) of ethanethiosulfonic acid, one of the closest analogs of allicin

$CH_3-CH_2-SO_2-S-CH_2-CH_3$ (VI) $CH_3-CH_2-SO-S-CH_2-CH_3$ (VII).

Of our alkyl esters of ethanethiosulfonic acid, the greatest antibacterial activity was possessed by the butyl ester which, with respect to action on Mycobacterium $B_5$ and Staphyloc. aureus, excelled ester (VI) by factors of 2 and 4, respectively.

The high toxicity and the considerable deactivation of certain of the esters (IV) by blood makes their use as medicinal agents difficult.

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Received July 12,1955



Lwow Polytechnical Institute


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• We take this opportunity to thank V. G. Lobotko, K. I. Beltyukova and S. I. Zelepukha for testing our preparations.

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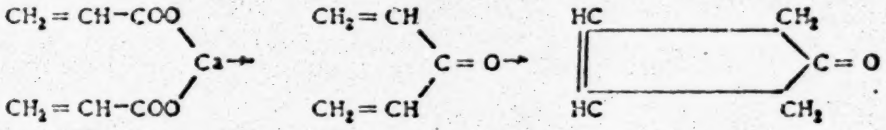
# SYNTHESIS OF 3-CYCLOPENTEN-1-ONE AND 2,5-DIMETHYL-3-CYCLOPENTEN-1-ONE •

B. N. Dashkevich

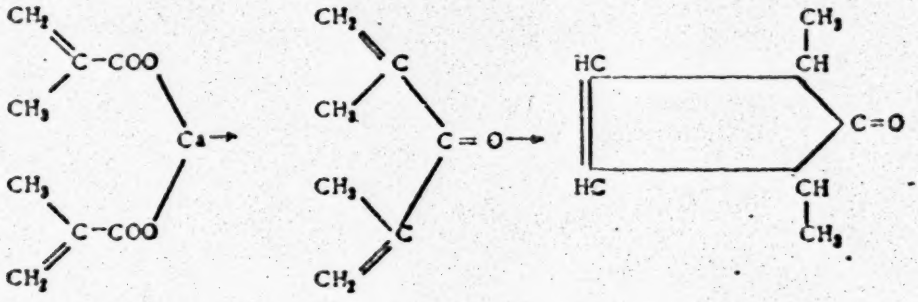
(Presented by Academician I. N. Nazarov, September 23,1955)

The cyclic pentenones described in the literature have a double bond in the α-position with respect to the carbonyl group. I. N. Nazarov worked out an interesting method for the preparation of unsaturated cyclic ketones with five-membered rings starting from vinyl-allyl ketones which, under the influence of phosphoric acid, undergo cyclization [1]. However, the pentenones obtained by this method always have the double bond in the ring in the α-position. It has been shown by us that symmetrical doubly unsaturated ketones when cyclized yield ketones with a double bond in the β-position. Turning attention to the formation of symmetrical saturated ketones by the well-known method of Williams and Friedel which involves the dry distillation of calcium or barium salts of carboxylic acids, we decided to test this method on the simplest acrylic acids in the hope that high temperature pyrolysis would lead to the cyclization of the doubly unsaturated ketones formed. By this means, we succeeded in preparing two cyclic ketones with the double bond in the β-position, namely, 3-cyclopenten-1-one and 2, 5-dimethyl-3-cyclopenten-1-one.

The process of preparation of the first ketone can be represented by the following:



An analogous mechanism can be assumed for the formation of the second ketone (2,5-dimethyl-3-cyclopenten-1-one):



3-Cyclopenten-1-one. The calcium salt was prepared from acrylic acid (b.p. 139-141°) by neutralization with calcium carbonate. After careful grinding, 50 g of this salt was mixed with 80 g of quartz sand. The thermal decomposition was carried out in a round-bottomed flask of refractory glass which was connected to an inclined condenser; the temperature was maintained at 450-500°. The process was concluded in 1 hour. 16.6 grams of a dark-colored pyrolyzate with a definite odor was collected in the receiver. After drying with sodium sulfate, the pyrolyzate was distilled. The initial boiling point was 82°. The final fraction, boiling at 133-135° and amounting to •• g, was collected and analyzed. Qualitative reactions showed that this was an unsaturated ketone. The yield was 26.9%.

• The present work was carried out jointly with V. K. Orlov and V. I. Tomchani.

•• Amount illegible in original text.

The molecular weight found (cryoscopically) was 84; calculated for $C_5H_6O$, 82. Bromine number: found 197; calculated for cyclopentenone 195.1 (for the corresponding aliphatic ketone, that is, for divinyl ketone, the calculated bromine number is 390.2). Found $d_4^{20}$ 0.9821, $n_D^{20}$ 1.4590.

Found %: C 67.9; H 7.3
Calculated %: C 68.2; H 7.6

The oxime melted at 50-51°.

In order to determine the position of the double bond, his ketone was subjected to oxidation with 1% solution of permanganate in a weakly alkaline medium. The oxidation product was acetonedicarboxylic acid, apparently since we isolated and identified acetone. We did not succeed in isolating products other than acetone. From this fact, it follows that the double bond was in the ring in the β-position with respect to the carbonyl group.

2,5-Dimethyl-3-cyclopenten-1-one. The meth crylic acid used as the starting material was prepared by us; b.p. 68-73°, $n_D^{20}$ 1.431. Its calcium salt was prepared by neutralization with calcium carbonate. Pyrolysis of the methacrylate was carried out in the same manner as used in the preceding synthesis. From 100 g of salt was obtained 45 g of pyrolyzate. From a second distillation of the pyrolyzate a fraction boiling at 156-157° was collected in an amount of 16.2 g which represents a yield of 31.2% ketone.

The molecular weight found (cryoscopically) was 113; calculated for $C_7H_{10}O$, 110. Bromine number: found, 148; calculated for the cyclic ketone $C_7H_{10}OBr$, 145.6. Found: $d_4^{20}$ 0.8971; $n_D^{20}$ 1.445. MR: found, 32.612; calculated 31.870 (exaltation, +0.742).

Found %: C 75.93; H 8.87
Calculated %: C 76.36; H 9.09

The semicarbazone melted at 160-162° and the 2,4-dinitrophenylhydrazone at 129°.

This unsaturated cyclic ketone was subjected to oxidation with permanganate in a weakly alkaline medium; this resulted in the formation of formic acid and acetone, which can be explained only by assuming that a double bond is in the β-position to the carbonyl group. The formation of formic acid can be explained by the splitting off of a methyl group, and the formation of acetone can be explained by the initial formation of acetonedicarboxylic acid and the decarboxylation of the latter. It would be impossible to explain the formation of acetone if the double bond were in the α-position

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Received June 10, 1955

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# ALKYLATION OF BENZENE BY BUTYLENES WITH A CATALYST WITH A BORON FLUORIDE BASE

Academician A. V. Topchiev, M. V. Kurashev and Ya. M. Paushkin

In previous work [1,2], we showed that, in the alkylation of benzene with propylene, a boron fluoride-orthophosphoric acid catalyst had greater activity than aluminum chloride, sulfuric acid, sulfuric acid-aluminum chloride complex, or boron fluoride monohydrate. In the present article is detailed an investigation of the alkylation of benzene with butylenes using a catalyst prepared from 88.7% orthophosphoric acid and boron fluoride. The method of preparation of a catalyst to be used with benzene and olefins is given in one of our previous articles [3]. The experimental method and the treatment of the reaction mixture has already been reported [4]; therefore, we proceed directly to a consideration of the results of the investigation.

**TABLE 1**

Alkylation of Benzene by n-Butene with Different Catalysts

| Catalyst | Composition of the mixture of benzene and alkylate, wt. % | | | Yield in % of theory | | |
|---|---|---|---|---|---|---|
| | Up to 160° | 160-180° | Above 180° | 160-180° | Above 180° | 172-174° |
| $H_3PO_4 \cdot BF_3$ | 38 | 58 | 4 | 91 | 6 | 85 |
| 88.7% $H_3PO_4 \cdot BF_3$ + 11.3% $H_2O \cdot BF_3$ | 38 | 58 | 4 | 91 | 6 | 85 |
| $H_2O \cdot BF_3$ | 38 | 59 | 3 | 93 | 5 | 87 |
| $AlCl_3$ | 43 | 43 | 14 | 67 | 15 | 56 |
| $AlCl_3 \cdot HSO_4$ | 47 | 29 | 24 | 46 | 38 | 41 |
| $H_2SO_4$ | 45 | 36 | 19 | 57 | 31 | 51 |

• Sec-Butylbenzene

In Table 1 are presented the experimental data on the alkylation of benzene by n-butene with different catalysts; the experiments were carried out at 50°, a mole ratio of benzene:n-butene of 2:1, and 15% catalyst in the reaction mixture. From the data presented it is seen that the boron fluoride-containing catalysts are more effective, not only for the alkylation of benzene by propylene, but also for the alkylation of benzene by n-butene. Thus, under identical alkylation conditions, the $H_3PO_4 \cdot BF_3$ and 88.7% $H_3PO_4 \cdot BF_3$ + 11.3% $H_2O \cdot BF_3$ catalysts gave an alkylate with a high content of the desired product – sec-butylbenzene (the fraction boiling at 172-174°) – up to 94%, while with $AlCl_3$, $H_2SO_4$, and $AlCl_3 \cdot HSO_4$ the sec-butylbenzene content was 68, 58, and 49% respectively.

In the experiments, attention was directed chiefly toward a clarification of the dependence of alkylate composition on the mole ratio of benzene: butene; furthermore, the effect of olefin addition rate, amount of catalyst, and reaction temperature on the alkylation process was established. The results are presented in Tables 2 and 3.

Effect of catalyst quantity. It was established by the investigation that during the alkylation of benzene by isobutylene with a catalyst concentration of 2% by weight of the benzene charged, the principal reaction is polymerization; although alkylation occurs, it proceeds considerably more slowly. Of the total amount of isobutylene entering into the reaction, 60% went to polymerization, and only 40% went to alkylation. Increasing the amount of catalyst to 5% increased the alkylation rate considerably; in this case, 97% of the isobutylene went to alkylation. With further increase in catalyst concentration, isobutylene polymerization nearly ceased, and simultaneously an increase in the tert-butyl-benzene content of the alkylate was observed; thus, for catalyst concentrations of 10, 15, and 25% the tert-butylbenzene content of the alkylate was 64, 67, and 71%, respectively; correspondingly, the yields of tert-butylbenzene were 49, 54, and 58%.

The general rules developed for the alkylation of benzene by propylene and isobutylene with a phosphoric acid-boron fluoride catalyst also apply to alkylation with n-butene. It should be noted that olefin polymerization proceeds to a lesser extent during alkylation with n-butene than during alkylation with isobutylene. In this case, 5% of catalyst is sufficient to suppress polymerization.

TABLE 2

Alkylation of Benzene by Isobutylene with Orthophosphoric Acid-boron Fluoride Complex Catalyst

| Experiment No. | Reaction temperature, °C | Isobutylene addition rate, hours$^{-1}$ | Mole ratio of $C_6H_6 : C_4H_8$ | Catalyst, % | Yield of fractions in % of theory | | | Total content of 169-170° fraction in alkylate* | Experiment No. | Reaction temperature, °C | Isobutylene addition rate, hours$^{-1}$ | Mole ratio of $C_6H_6 : C_4H_8$ | Catalyst, % | Yield of fractions in % of theory | | | Total content of 160-170° fraction in alkylate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 160-180° | Above 180° | 169-170° | | | | | | | 160-180° | Above 180° | 169-170° | |
| 1 | 50 | 6 | 2:1 | 5 | 52 | 34 | 46 | 60 | 9 | 50 | 20 | 1 : 1 | 15 | 40 | 43 | 36 | 48 |
| 2 | 50 | 6 | 2:1 | 10 | 55 | 31 | 49 | 54 | 10 | 50 | 20 | 2 : 1 | 15 | 59 | 29 | 54 | 67 |
| 3 | 50 | 6 | 2:1 | 15 | 59 | 29 | 54 | 67 | 11 | 50 | 20 | 4 : 1 | 15 | 71 | 20 | 64 | 77 |
| 4 | 50 | 6 | 2:1 | 25 | 63 | 26 | 58 | 71 | 12 | 50 | 20 | 8 : 1 | 15 | 71 | 20 | 65 | 78 |
| 5 | 50 | 12 | 2:1 | 15 | 59 | 29 | 54 | 67 | 13 | 0 | 20 | 2 : 1 | 15 | 29 | 50 | 26 | 36 |
| 6 | 50 | 20 | 2:1 | 15 | 59 | 29 | 54 | 67 | 14 | 10 | 20 | 2 : 1 | 15 | 44 | 39 | 37 | 48 |
| 7 | 50 | 30 | 2:1 | 15 | 55 | 32 | 50 | 64 | 15 | 20 | 20 | 2 : 1 | 15 | 49 | 36 | 45 | 60 |
| 8 | 50 | 60 | 2:1 | 15 | 54 | 32 | 48 | 62 | 16 | 80 | 20 | 2 : 1 | 15 | 69 | 21 | 63 | 76 |

* Tert-butylbenzene

TABLE 3

Alkylation of Benzene by n-Butene with an Orthophosphoric Acid-boron Fluoride Complex

| Experiment No. | Reaction temperature, °C | n-Butene addition rate, hours$^{-1}$ | Mole ratio of $C_6H_6 : C_4H_8$ | Catalyst, % | Yield of fractions, % of theory | | | Total content of 172-174° fraction in alkylate* |
|---|---|---|---|---|---|---|---|---|
| | | | | | 160-180° | Above 180° | 172-174° | |
| 1 | 50 | 6 | 2 : 1 | 5 | 87.4 | 9 | 81 | 91 |
| 2 | 50 | 6 | 2 : 1 | 10 | 87.7 | 9.8 | 81 | 91 |
| 3 | 50 | 3 | 2 : 1 | 15 | 91.0 | 6.3 | 85 | 94 |
| 4 | 50 | 6 | 2 : 1 | 25 | 91.3 | 6.3 | 85 | 94 |
| 5 | 50 | 20 | 2 : 1 | 15 | 91.0 | 6.3 | 85 | 94 |
| 6 | 50 | 30 | 2 : 1 | 15 | 91.0 | 6.3 | 85 | 94 |
| 7 | 50 | 10 | 2 : 1 | 15 | 76.6 | 16.7 | 71 | 82 |
| 8 | 50 | 20 | 2 : 1 | 15 | 83.4 | 11.8 | 79 | 88 |
| 9 | 50 | 30 | 2 : 1 | 15 | 91.0 | 6.3 | 85 | 94 |
| 10 | 50 | 30 | 4 : 1 | 15 | 92.0 | 6.1 | 85 | 94 |
| 11 | 10 | 30 | 2 : 1 | 15 | 79.3 | 14.9 | 74 | 83 |
| 12 | 20 | 30 | 2 : 1 | 15 | 89.4 | 7.5 | 82 | 91 |

* Sec-butylbenzene

Effect of olefin addition rate. An increase in addition rate leads, as in propylene alkylation, to a decrease in the yield and content of monoalkylbenzenes; thus, with an isobutylene addition rate of 15 liters/hour (40 hours$^{-1}$), the

yield of tert-butylbenzene was 50 % of theory and the content in the alkylate was 64%, and for n-butene at 30 liter/hour (60 hours$^{-1}$) the yield of sec-butylbenzene was 71% of theory and the content in the alkylate was 82%.

Effect of mole ratio of components. An increase in the yield of monoalkylbenzenes can be obtained by increasing the mole ratio of benzene: isobutylene. An increase in the ratio of benzene: isobutylene from 1:1 to 2:1 increased the yield of alkylate from 83 to 88% of theory and the content of tert-butylbenzene in the alkylate from 48 to 67%; at a ratio of 4:1, the yield was 91% of theory and the tert-butylbenzene content of the alkylate was 77%. A further increase in the mole ratio benzene: isobutylene had almost no effect on the alkylation process; at a ratio of 6:1, the alkylate yield was 91% of theory and the tert-butylbenzene content of the alkylate was 78%.

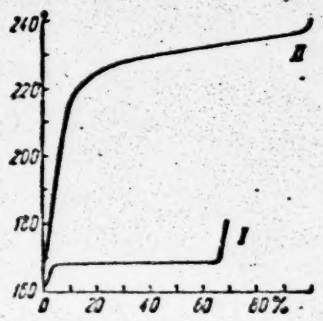


Fig. 1. Distillation of alkylate obtained by alkylation of benzene with isobutylene (2:1). I)Monoalkylation product (160-180° fraction); II)dialkylation product 180-237° fraction).

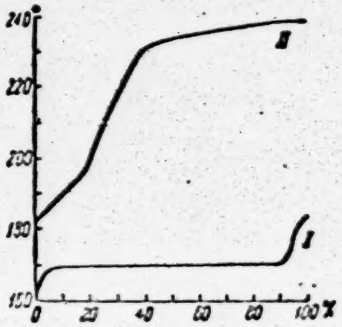


Fig. 2. Distillation of the alkylate obtained at a mole ratio of benzene: n-butene of 2:1. I) Monoalkylation product (160-180° fraction); II)dialkylation product (182-238° fraction).

Comparing the alkylation of benzene with propylene and with isobutylene, we note that the yield of propylene alkylate exceeds by 5-8% the yield of isobutylene alkylate and the isopropylbenzene content of the alkylate in the individual cases exceeds by 40% (1:1) the tert-butylbenzene content. The yield of polyalkylbenzenes during isobutylene alkylation is two times, and in certain cases (6:1 and 8:1) 3-4 times, higher than during propylene alkylation. This indicates the effect of molecular weight and structure of the olefin on the yield of reaction products.

It is interesting that the yield of alkylate was higher in the alkylation of benzene with n-butene than with isobutylene or propylene. The explanation of this could be that the rate of secondary alkylation is slower for n-butene than for isobutylene or propylene. The yield of alkylate is also affected by the considerable tendency of isobutylene toward polymerization; evidently, in this case the difference in the rates of formation of alkylbenzenes and polymers is small, and, therefore, polymer is found in the alkylate.

Composition of products of the alkylation of benzene with butenes. Alkylates obtained at mole ratios of benzene: butene of 2:1 and 1:1 were used in the investigation of the composition of alkylate from butene alkylation. Distillation curves of the alkylates are presented in Figures 1 and 2.

Alkylate obtained at a mole ratio of benzene: isobutylene of 2:1 comprised 61.4% tert-butylbenzene, 6.1% intermediate fraction, and 32.1% of a fraction which was almost pure 1,4-di-tert-butylbenzene. The remainder of the isobutylene alkylate (boiling above 180°) comprised chiefly di-tert-butylbenzene – 225 to 237° fraction. This fraction was subjected to recrystallization to yield white crystals boiling at 235-236° at 756 mm Hg, melting at 78°, and having a molecular weight of 190; according to the literature [5], these properties correspond to 1,4-di-tert-butylbenzene. The residue boiling above 237° apparently comprised di-tert-butylbenzene and products of hydro-dehydropolymerization of isobutylene. The formation of tri-tert-butylbenzene was not observed.

The alkylate from n-butene contained considerably more (94%) monoalkylbenzene than did the alkylate from isobutylene (67%) and even propylene (90.0%). The alkylation of benzene with n-butene proceeded better than alkylation with propylene under the same conditions; the yield of polymerization products and polyalkylbenzenes was insignificant.

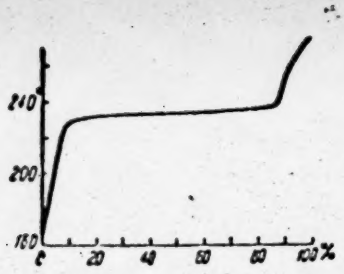


Figure 3. Distillation of the fraction boiling above 180° from the alkylation of benzene with n-butene at a mole ratio of 1:1.

Polymerization was not observed at a mole ratio of benzene : n-butene of 2:1, an alkylation temperature of 50°, an olefin addition rate of 7 liters/hour, and 23.4 g of catalyst. The residue from the distillation of the alkylate was a mixture of mono- and poly sec-butylbenzenes. With the aim of determining the nature of the poly-sec-butylbenzene fraction, the fraction boiling above 180°, obtained at a mole ratio of benzene: n-butene of 1:1, was distilled (see Figure 3). 4.3% of a mono-sec-butylbenzene fraction, 73.6% of a di-sec-butylbenzene fraction and 22.1% of an intermediate fraction were obtained.

In order to obtain purer hydrocarbons, the di-sec-butylbenzene fraction (230-240°) was washed with sulfuric acid, neutralized and again distilled; a fraction was obtained in 95% yield having b.p. 235-236°, $d_4^{20}$ 0.8580, $n_D^{20}$ 1.4885, and a molecular weight of 190. Di-sec-butylbenzene (1, 4), according to the literature [5], has the following constants: $d_4^{20}$ 0.8573 $n_D^{20}$ 1.4884; b.p. 237°.

In order to determine the position of the alkyl groups, the fraction was oxidized with alkaline potassium permanganate; the yield of oxidation products was 40%; oxidation with 25% nitric acid at 90-100° for 25 hours gave 60% yield of white crystals which, after recrystallization, melted with decomposition at 300°. The dimethyl ether prepared from this dicarboxylic acid melted at 140°. Other acids were not found.

Thus, it can be considered as demonstrated that the acid obtained was terephthalic acid and that the original hydrocarbon was 1,4-di-sec-butylbenzene.

The 240-274° fraction and the material boiling above 274° was a mixture comprising di-sec-butylbenzene, products of the polymerization of n-butene, and, possibly, tri-sec-butylbenzene. Owing to the small amount of the fraction boiling above 274°, it was not possible to determine whether tri-sec-butylbenzene was present. Therefore, an experiment on the alkylation of 1,4-di-sec-butylbenzene with n-butene at 50° was conducted. The results of the investigation showed that, under these conditions, 1-4-di-sec-butylbenzene is not alkylated by n-butene. The reaction products were a complex mixture of hydrocarbons formed as a result of polymerization, hydro-dehydropolymerization of n-butene, and also cracking.

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Received November 14, 1955

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# SYNTHESIS OF PEPTIDES CONTAINING α-HYDROXY-α-AMINO ACID RESIDUES

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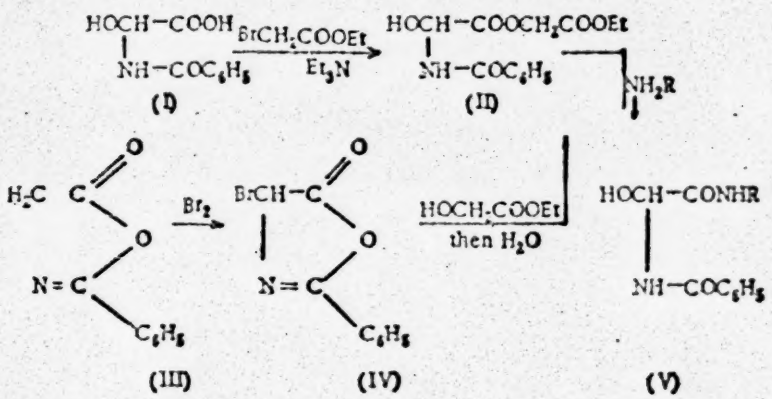
G. A. Ravdel and E. S. Chaman

It has long been known that α-hydroxy-α-amino acids, along with other amino acids, enter into the composition of the molecules of certain natural peptides (the majority of the ergoalkaloids, the antibiotic lycomarasmine) [1-3]. However, up to the present, the synthesis of peptides of this type has been difficult, since α-hydroxy-α-amino acids are practically unavailable owing to the absence of methods for their synthesis. Only after the recent discovery by us [4] and simultaneously by I. L. Knunyants and co-workers of a method for the synthesis of N-acylated α-hydroxy-α-amino acids did it become possible to approach a solution of the question of a route for the introduction of α-hydroxy-α-amino acids into peptides.

With the aim of synthesizing peptides in which α-hydroxy-α-amino acids are the N-terminal amino acids, we investigated the recently described method for the preparation of peptides through the so-called "activated esters" [6] and also by the well-known oxazolinone method. Both of these methods permitted easy synthesis of the desired peptides, which were prepared in the form of various derivatives according to schemes 1 and 2.

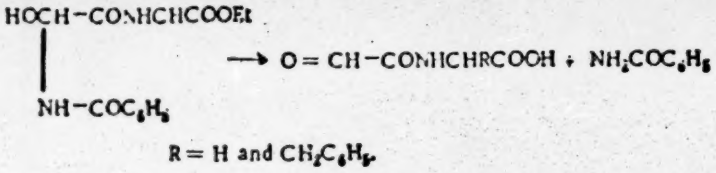
Scheme 1




In order to determine the applicability of the first of the above-mentioned methods, it was first necessary to study the possibility of preparing sufficiently activated esters of α-hydroxy-α-amino acids. This possibility was verified using the carbethoxymethyl ester of N-benzoylhydroxyglycine (II). Attempts to prepare it from N-benzoylhydroxyglycine (I) and $BrCH_2COOEt$ under the conditions described for the carbethoxymethyl ester of hippuric acid [6] only led to unsatisfactory results — the yield of ester (II) did not exceed 4-5%. However, this ester was successfully synthesized in considerably better yield from 4-bromo-2-phenyloxazolinone-5-(IV), which, in turn, was prepared by bromination of 2-phenyloxazolinone-5 (III) [4]. Starting from the previously established fact [7] that cleavage of the oxazolinone ring of 4-bromo-2-phenyloxazolinone-5-(IV) proceeds faster than substitution of the bromine atom, it would be expected that ester (II) would be formed in satisfactory yield by the action of $HOCH_2COOEt$ and then water on the oxazolinone. Actually, ester (II) was synthesized by this means in 40% yield.

Clarification of the possibility of using ester (II) for the synthesis of peptides and the study of reaction conditions were carried out with benzylamine; it was shown that the formation of the amide bond proceeds under very mild conditions, and the amide (Va) was obtained in 86% yield. Formation of the amide bond was also easily achieved by the action of esters of glycine and of phenylalanine on ester (II), leading to the formation of derivatives of dipeptides (Vb) and (Vc). The latter was characterized by subjecting it to acid and alkaline hydrolysis. Boiling with concentrated HCl for 4 hours led to cleavage to benzoic, glyoxylic, and α-amino acids. Upon agitation with 0.5-1 N NaOH at 20°, saponification of the ester group and rupture of the hydroxyamino acid residue resulted, but the

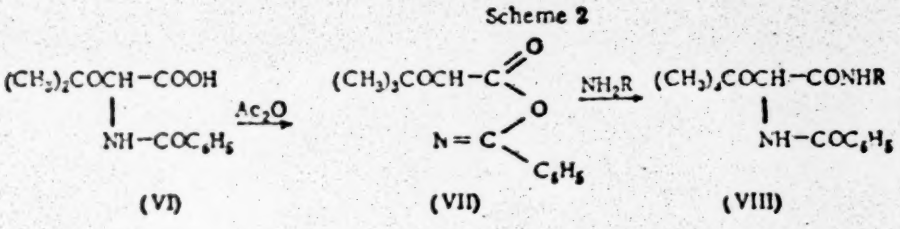
amide bond remained untouched resulting in the formation of N-glyoxylylamino acids which were isolated in the form of the 2,4-dinitrophenylhydrazones:



R = H and $CH_2C_6H_5$.

The second method of introducing α-hydroxy-α-amino acids into peptide molecules (through the oxazolinone) was studied using 4-tert-butoxy-2-phenyloxazolinone-5 (VII), which was prepared by the usual method from the previously described [7] N-benzoyl-O-tert-butoxyglycine (VI). Conditions for the interaction of this oxazolinone with compounds containing an amino group were first investigated using aniline, which resulted in the formation of anilide (VIIIa). Reactions with esters of glycine and phenylalanine, leading to the formation of derivatives of peptides (VIIIb) and (VIIId), proceeded under similar conditions.

Scheme 2



(VI) (VII) (VIII)

VIIIa: R = $C_6H_5$; VIIIb: R = $CH_2COOEt$; VIIIc: R = $CH_2COOH$;
VIIId: R = $CH(CH_2C_6H_5)COOEt$; VIIIe: R = $CH(CH_2C_6H_5)COOH$.

Upon alkaline hydrolysis (1 N NaOH, 20-25°), both of these compounds behaved differently from the above-described derivatives of peptides of type (V) which contained an α-hydroxy-α-amino acid residue with a free hydroxyl group. In distinction from the latter, with compounds of type (VIII) only saponification of the ester groups occurred, owing to which the corresponding dipeptides with free carboxyl groups (VIIIc) and (VIIIe) were successfully isolated. Compounds of the types (V) and (VIII) underwent the same acid hydrolysis, however.

## EXPERIMENTAL

1. Preparation of (II). To 5 g of (III) in 30 ml of dry dichloroethane was added dropwise, at 5-8°, 2.5 g of bromine in 7 ml of dichloroethane. The precipitated bromo derivative of (III) was filtered and washed with 15-20 ml of dichloroethane [4, 7]. To the solution of (IV) was added, at 0-2°, over a period of 7-10 minutes, a solution of 1.7 g of $HOCH_2COOEt$ in 5 ml of dichloroethane, and the mixture was stirred at 0-2° for an hour. 15 ml of water was then added, the mixture was stirred for 20 minutes, and the dichloroethane solution was washed twice with water, and evaporated under vacuum. The residue was then triturated three times with water (8-10 ml) and once with 10 ml of 5% $NaHCO_3$, and the residue was then filtered and washed with ether. The yield was 1.75 g (40%); m.p. 99-102°. The (II) thus obtained could be used for the synthesis of peptides without further purification. The pure preparation (m.p. 111-113°) was obtained by crystallization from water.

| | | |
|---|---|---|
| | Found %: | C 55.58; H 5.19; N 4.85 |
| $C_{13}H_{15}O_4N$. | Calculated %: | C 55.51; H 5.37; N 4.97 |

2. Preparation of (Va). To 0.45 g of (II) in 3 ml of dry ethylacetate was added 0.17 g of benzylamine, and the mixture, with periodic stirring, remained at 20° for 3 hours. The precipitate was filtered and washed with ethyl acetate. The yield was 0.39 g (86%); m.p. 152-153° with decomposition (from alcohol).

| | | |
|---|---|---|
| | Found %: | C 67.79; H 5.62; N 10.05 |
| $C_{16}H_{16}O_3N_2$. | Calculated %: | C 67.58; H 5.66; N 9.85 |

0.15 g of (Va) was stirred for 3 hours with 2.5 ml of 0.5 N aqueous-alcoholic NaOH; the mixture was acidified and filtered, and the benzylamide of glyoxylic acid was isolated as the 2,4-dinitrophenylhydrazone. M.p. 185-187° with decomposition (from alcohol).

Found %: C 52.55; H 3.82; N 20.34
$C_{18}H_{13}O_5N_5$. Calculated %: C 52.46; H 3.81; N 20.40

3. Preparation of (Vb). A suspension of 0.45 g of HCl·$NH_2CH_2COOEt$ in 5 ml of $CH_3CN$ was warmed for 5 minutes at 50° with 0.31 g of $Et_3N$. The mixture was cooled to 20°, and 0.6 g of (II) was added; after standing, with periodic stirring, for 4 hours, it was filtered and evaporated to dryness under vacuum at 25-30°. The residue was triturated with 2 ml of water, filtered, and washed with water. The yield was 0.34 g (56%); m.p. 127-129° (from water).

Found %: C 55.42; H 5.79; N 9.99
$C_{13}H_{16}O_4N_2$. Calculated %: C 55.67; H 5.75; N 9.99

0.4 g of (Vb) was stirred for 2.5 hours with 3 ml of 1 N NaOH. After filtering off 0.11 g (63%) of benzamide, N-glyoxylylglycine was isolated from the acidified filtrate as the 2,4-dinitrophenylhydrazone. Weight, 0.19 g; m.p. 214-215° (from alcohol).

Found %: C 38.90; H 2.98; N 22.38
$C_{10}H_8O_7N_6$. Calculated %: C 38.57; H 2.92; N 22.50

4. Preparation of (Vc). 0.25 g of (II) was dissolved at 30-35° in 1.5-2 ml of dry ethyl acetate, 0.3 g of the ethyl ester of phenylalanine was added, and the mixture was maintained for 16 hours at 20°. 3-4 ml of ethyl acetate was added, and the mixture was washed with 2% HCl, and water, dried with $Na_2SO_4$, and evaporated under vacuum. Compound (Vc) was an oil which did not distill under vacuum without decomposition. Upon alkaline hydrolysis (stirring for 3 hours with 1 ml of 0.5 N NaOH), it formed glyoxylylphenylalanine which was isolated as the 2,4-dinitrophenylhydrazone; m.p. 198-200° with decomposition (from alcohol).

Found %: C 50.90; H 3.76; N 17.75
$C_{17}H_{15}O_7N_5$. Calculated %: C 50.85; H 3.76; N 17.45

5. Preparation of (VIIIa). 0.5 g of the monohydrate of compound (VI) [7] was heated for 2 hours at 90-95° (bath temperature) with 10 ml $Ac_2O$. The latter was distilled off under vacuum, and oxazolinone (VII) was used for further preparations without purification. It was dissolved in 5 ml of dichloroethane, 0.35 ml of aniline was added, the mixture was warmed for 2 hours at 30-40°, filtered, evaporated under vacuum, and the residue triturated with ether. 0.15 g (25%) of anilide (VIIIa) was obtained; it was crystallized twice from $C_2H_5OH$ and twice from $CH_3OH$. M.p. 176-177°.

Found %: C 70.05; H 6.69; N 8.75
$C_{15}H_{22}O_3N_2$. Calculated %: C 69.93; H 6.79; N 8.58

6. Preparation of (VIIIc). Oxazolinone (VII) prepared from 1g of the monohydrate of compound (VI) under the conditions of Experiment 5 was dissolved in 5 ml of dichloroethane, and 1.04 g HCl·$NH_2COOEt$ and 0.7 g $Et_3N$ in 10 ml of dichloroethane was added. On the following day, the precipitate was filtered off and washed with dichloroethane; the solution was washed with water, 5% HCl, 4% $NaHCO_3$, and again with water, dried with $Na_2SO_4$, and evaporated under vacuum. 0.35 g (28%) of compound (VIIIb) with an m.p. of 161-163° (from acetone) was obtained.

Found %: C 60.90; H 7.26; N 8.37
$C_{17}H_{24}O_5N_2$. Calculated %: C 60.70; H 7.19; N 8.32

0.33 g of (VIIIb) was stirred for 3 hours at 25° with 4 ml of 1 N NaOH. The resulting colorless needles were filtered, acidified, and maintained at 2-3° for 8-10 hours. Peptide (VIIIc) was crystallized from water as the monohydrate with an m.p. of 104-109°.

Found %: C 55.62; H 6.82; N 8.48
$C_{15}H_{20}O_5N_2 \cdot H_2O$. Calculated %: C 55.21; H 6.64; N 8.58

7. Preparation of (VIIIe). Oxazolinone (VII) prepared from 1 g of monohydrate of compound (VI) under the conditions of Experiment 5 was dissolved in 5 ml of dichloroethane, and 1.4 g of the ethyl ester of phenylalanine was added. The next day, the solution was washed with 5% HCl and water, after which the dichloroethane was distilled off under vacuum. The remaining oil (compound VIIId) was hydrolyzed by stirring for 3 hours at 20° with 6 ml of 1 N NaOH. The solution was extracted with ether and acidified. The oil was separated, dissolved in 8% $NaHCO_3$, again acidified, and the liberated viscous oil was mixed well with water. This operation was repeated twice. Peptide (VIIIe) was a solid material melting at 64-68°.

Found %: C 66.30; H 6.49; N 6.91; mol. wt. (titration) 392

$C_{22}H_{26}O_5N_2$. Calculated %: C 66.31; H 6.57; N 7.03; mol. wt. 398.4

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Received September 24, 1955



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* T. p. = C.B. Translation pagination.

# PREPARATION OF POTASSIUM NITRODICHLOROMONOAMMINOPLATOATE

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(Presented by Academician A. N. Frumkin, September 29, 1955)

Potassium nitrodichloromonoammminoplatoate, $K[PtNH_3ClNO_2Cl]$, has recently attracted the attention of investigators in connection with work undertaken with the aim of establishing the quantitative nature of the trans-effect of individual substituents, especially after publication of the article by A. D. Gelman and E. F. Karandashova, "The Reaction of Potassium Triacidomonoammininoplatoates $K[PtNH_3Cl_2X]$ with Pyridine", [1].

The authors studied the action of pyridine on the salts $K[PtNH_3ClXCl]$, formed according to the reaction $K[PtNH_3Cl_3] + KX = K[PtNH_3ClXCl] + KCl$, without liberating the salts from solution. In order to remove all doubts as to the course of the reaction, it was necessary to prepare the starting monoammine, particularly $K[PtNH_3ClNO_2Cl]$, in the crystalline form. The corresponding chloro and bromo monoammines were easily isolated by these same authors. The synthesis of $K[PtNH_3ClNO_2Cl]$ has been attempted by a series of investigators, but without success. Recently, we succeeded in obtaining this compound. Its synthesis was carried out according to the following example.

A 1.1627 g sample of potassium trichloromonoamminoplatoate, $K[PtNH_3Cl_3]$, was dissolved in 30 ml of water, and the solution was heated on a water bath. To the heated solution was added 0.2242 g of $NaNO_2$ dissolved in the minimum volume of water. The amount of $NaNO_2$ required for the reaction was determined on the basis that 1 mole of $NaNO_2$ is required per mole of the salt $K[PtNH_3Cl_3]$.

Immediately after the addition of the $NaNO_2$, the color of the solution changed from orange to light yellow, indicating that the $NO_2$ group has been introduced into the inner sphere:

$$K[PtNH_3Cl_3] + NaNO_2 = K[PtNH_3ClNO_2Cl] + NaCl. \qquad (A)$$

Inasmuch as $K[PtNH_3ClNO_2Cl]$ and NaCl are both easily soluble salts, our further problem was the separation of the complex ion $[PtNH_3ClNO_2Cl]^{-1}$ in the form of the insoluble salt

$$[Pt(NH_3)_4][PtNH_3ClNO_2Cl]_2. \qquad (I)$$

With this aim, we treated the solution with tetraamminoplatinum chloride. The reaction proceeded according to the equation

$$2K[PtNH_3ClNO_2Cl] + [Pt(NH_3)_4]Cl = [Pt(NH_3)_4][PtNH_3ClNO_2Cl]_2\downarrow + KCl,$$

and, as a result, a yellowish orange precipitate (I) was formed. It was filtered, carefully washed with cold water, and dried. 1.0423 g of the salt was obtained.

| | | | |
|---|---|---|---|
| | Found %: | Pt 63.90; 63.46; 63.25; | Cl 16.27 |
| $[Pt(NH_3)_4][PtNH_3ClNO_2Cl]_2$. | Calculated %: | Pt 63.54; | Cl 15.41 |
| | Mol. wt. | 921.6 | |

In order to convert the obtained salt (I) to potassium nitrodichloromonoammminoplatoate, it was necessary to carry out an exchange reaction between this salt and potassium chloroplatinite:

$$[Pt(NH_3)_4][PtNH_3ClNO_2Cl]_2 + K_2[PtCl_4] = [Pt(NH_3)_4][PtCl_4]\downarrow + 2K[PtNH_3ClNO_2Cl] \quad (II)$$

In order to obtain the pure salt (II), it was necessary to control strictly the ratio of the reacting substances during the exchange reaction. It was calculated that 0.8204 g of salt (I) required 0.3698 g of $K_2[PtCl_4]$. Salt (I) was ground in an agate mortar with the precisely weighed amount of potassium chloroplatinite; the powder was then transferred to a beaker, and 3 ml of hot water was added to it. The potassium nitrodichloromonoammino-platoate (II), formed as a result of the exchange reaction, went into solution, but a green Magnus salt precipitated. After separation of the precipitate, the filtrate was evaporated with slight warming on a water bath and then at room temperature.

After evaporation for two days, a yellow, sticky, lumpy, solid substance remained in the dish. These lumps were moistened with alcohol and ground with a glass rod.

As a result of repeatedly carrying out this operation, the material was converted into a yellow crystalline powder. The product obtained weighed 0.4710 g. It was dried for 3 days over calcium chloride in a desiccator, and was then analyzed.

| | | | |
|---|---|---|---|
| | Found %: | Pt 50.64; 50.90; 50.68; | Cl 18.85 |
| $K[PtNH_3ClNO_2Cl]\cdot H_2O$. | Calculated %: | Pt 50.53; | Cl 18.38 |
| | Mol. wt. 386.3. | | |

The salt lost 2.09% in weight in the drying cabinet at 110°. The theoretical loss of half the water of crystallization is 2.33%. Upon standing in air, the salt again absorbs moisture, and loses it on drying. The loss of water proceeded very slowly. The salt dried at 110° was analyzed.

| | | |
|---|---|---|
| | Found %: | Pt 51.92; 51.99 |
| $K[PtNH_3ClNO_2Cl]\cdot {}^1/_2H_2O$. | Calculated %: | Pt 51.73 |

Analysis of the salt dried at 150° gave:

| | | | |
|---|---|---|---|
| | Found %: | Pt 52.44; 52.71; 53.09; | Cl 19.55 |
| Anhydrous $K[PtNH_3ClNO_2Cl]$. | Calculated %: | Pt 53.00; | Cl 19.28 |

Thus, it can be concluded that the salt completely loses water at 150°, but the substance begins to melt at this temperature. The salt is easily soluble in water.

The action of pyridine on an aqueous solution of $K[PtNH_3ClNO_2Cl]$ yields the cis-diammine $[PyNO_2NH_3ClPt]$ – a white crystalline material. The reaction proceeds according to the equation:

$$K\begin{bmatrix} NH_3 & & NO_2 \\ & Pt & \\ Cl & & Cl \end{bmatrix} + Py = \begin{bmatrix} NH_3 & & NO_2 \\ & Pt & \\ Py & & Cl \end{bmatrix} + KCl$$

0.4243 g of $K[PtNH_3ClNO_2Cl]\cdot {}^1/_2H_2O$ was dissolved in 10 ml of water and the calculated amount of pyridine was added (0.095 ml). Formation of a precipitate was initiated after about 5 minutes by rubbing the wall of the beaker with a glass rod. After 12 hours, the precipitate was filtered, washed well with cold water, and dried in a desiccator. The material obtained weighed 0.1684 g.

| | | | |
|---|---|---|---|
| | Found %: | Pt 52.13; 52.21; | Cl 9.40; 9.32 |
| $[PyNO_2NH_3ClPt]$. | Calculated %: | Pt 52.37; | Cl 9.52 |

In both composition and properties, the compound appeared to be identical with $[PyNO_2NH_3ClPt]$, previously [1] obtained by the action of pyridine on the salt $K[PtNH_3ClNO_2Cl]$, which was formed in solution by Reaction (A).

This indicates, apparently, that the reaction of $K[PtNH_3ClNO_2Cl]$ with pyridine proceeds in a completely analogous manner both with a solution of the salt which was previously isolated in the crystalline state and with a solution obtained without previous separation of the salt in the solid form.

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Received September 21, 1955

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# POLYMORPHISM OF BERYLLIUM FLUORIDE

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A. V. Novoselova and Yu. P. Simanov

In 1926, Goldschmidt [1] proposed the use of "structural models" for the study of the structures and transformations of complex oxides, particularly silicates. According to Goldschmidt, a satisfactory model is a substance having a formula analogous to the original substance and constructed from atoms or ions relatively close in dimensions and polarizing properties but differing in charge. Inasmuch as the fluoride ion has a radius almost equal to that of oxygen but only half the charge of oxygen, many fluorides are twice weakened models of oxides. Fluorides are characterized by lower hardness, lower refractive indices, and greater solubility than the corresponding oxides. Owing to the closeness of the dimensions of the ions Be (0.34 A) and Si (0.39 A), on the one hand, and of fluorine (1.33 A) and oxygen (1.32 A), on the other, beryllium fluoride can serve as a structural model of silicon dioxide. The first structural analogy of beryllium fluoride with silicon dioxide was discovered experimentally by Brandenberger [2]. He found that beryllium fluoride prepared by thermal decomposition of $(NH_4)_2BeF_4$ had a tetragonal lattice of the low temperature cristobalite type with the parameters: a = 6.60 kX, b = 6.74 kX, and b/a = 1.02.

During an investigation of the system $NaF - BeF_2$ in our laboratory, a new modification of $BeF_2$, having a hexagonal lattice analogous to low temperature quartz, was found [3]. The lattice parameters of this modification are: a = 4.72 kX, b = 5.18 kX, and b/a = 1.10.

Roy and coworkers [4] established that at 200° the low temperature quartzitic form of $BeF_2$ is converted to a modification analogous to high temperature quartz with a = 4.77 kX, b = 5.24 kX, and b/a = 1.09.

In the present work, we carried out a thermographic and x-ray investigation of tetragonal beryllium fluoride having the structure of cristobalite. We prepared the cristobalitoid $BeF_2$ by thermal decomposition of ammonium fluoroberyllate using the conditions indicated in the work of A. V. Novoselova and M. Ya. Avetkova [5]. In the thermal investigation, we inserted a platinum crucible containing the beryllium fluoride into a tightly closed steel cylinder, which protected the preparation from moisture. Recording of the heating curve was carried out using a differential thermocouple in the pyrometer of N. S. Kurnakov. Magnesium oxide was used as the standard.

The x-ray investigation of beryllium fluoride was carried out in phosphate glass capillaries. Beryllium fluoride reacts appreciably with ordinary glass and with quartz glass. Having phosphate glass at our disposal permitted carrying out the investigation of samples at up to 530°. High temperature exposures were made with a 190.05 mm "Unicam" camera. A description of this camera is given in reference [6].

In Figure 1 is depicted the heating curve of the cristobalite form of beryllium fluoride.

Distinct endothermic effects are observed at 130 and 545°. In addition, an effect at about 400° was also observed on some of the thermograms. The x-ray investigation showed that conversion of tetragonal $BeF_2$ into the cubic form occurred at 130°.

All of the lines of the new modification were indicative of a cubic, face-centered lattice with a = 6.78 kX, Z = 8. This new modification of $BeF_2$ is analogous to the high temperature form of cristobalite having a = 7.12 kX and Z = 8. In Table 1 is presented a collection of the interplanar distances and facial indices of the new modification of $BeF_2$ and $\beta$-cristobalite.

As already stated above, on the heating curves of $BeF_2$ we observed, in certain cases, a thermal effect at

about 400°; however, the x-ray investigation did not uncover any new modification. Only the lines of the cubic form of $BeF_2$ were present on the radiograms obtained at 400, 470, and 530°.

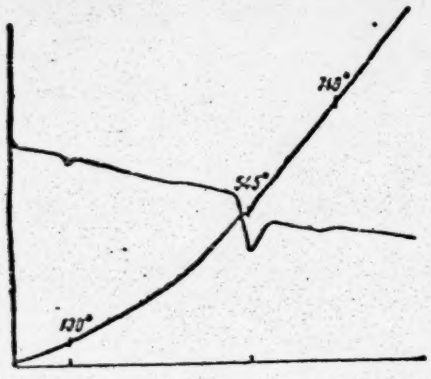


Fig. 1. Heating curve of the cristobalite form of $BeF_2$.

TABLE 1

| High temperature cristobalite form of $BeF_2$ | | | | $SiO_2$, β-cristobalite | |
|---|---|---|---|---|---|
| Intensity | d, found | d, calc. | Indices, hkl | d | Indices, hkl |
| 10 | 3.916 | 3.916 | 111 | 4.142 | 111 |
| 3 | 2.406 | 2.396 | 220 | 2.527 | 220 |
| 4 | 2.047 | 2.047 | 311 | — | — |
| 6 | 1.959 | 1.958 | 222 | 2.072 | 222 |
| 2 | 1.696 | 1.695 | 400 | 1.781 | 400 |
| 4 | 1.558 | 1.55 | 331 | 1.639 | 331 |
| 2 | 1.386 | 1.386 | 422 | 1.456 | 422 |
| 2 | 1.200 | 1.200 | 440 | 1.262 | 440 |
| 3 | 1.148 | 1.146 | 531 | 1.204 | 531 |

The thermal effect observed on the heating curve at 545° corresponds to the beginning of melting of beryllium fluoride. $BeF_2$ is hygroscopic, and therefore, it is impossible to carry out an observation on the heating process in an open crucible. We observed the process of fusion of $BeF_2$ through the wall of a quartz ampoule, into which was inserted a platinum crucible containing the beryllium fluoride. The ampoule was heated in a crucible furnace, the internal surface of which was strongly illuminated by a lamp with a reflector. Observation showed that only a part of the beryllium fluoride melted at 545°; the main mass of the material remained solid in spite of continued heating of the furnace. A second melting proceeded at about 740°, but the melt remained slightly turbid even at this temperature.

The stepwise melting process of beryllium fluoride indicates that the process of transformation of some modifications of beryllium fluoride proceeds slowly; therefore, $BeF_2$ can be considered as a pseudo one-component system.

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Received October 3, 1955

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# ALKYLATION OF BENZENE WITH AMYLENES USING A CATALYST BASED ON BORON FLUORIDE

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In previous communications [1-3], we showed that the complex of orthophosphoric acid with boron fluoride has a high activity for the alkylation of benzene with propylene and butylenes. In the present investigation, a compound prepared by the saturation of 88.7% orthophosphoric acid with boron fluoride was used as the catalyst. It was established by us that saturation of aqueous orthophosphoric acid with boron fluoride results in the formation of two complex compounds — boron fluoride monohydrate and a complex of orthophosphoric acid in $BF_3$. Preparation of the catalyst was carried out by the method usually used in our investigations. Briefly, it included passage of purified boron fluoride through molten crystalline orthophosphoric acid using a glass capillary. As the prepared complex became liquid, heating was discontinued and saturation was continued at 20°. The catalyst prepared under these conditions contained 88.7% of the complex $H_3PO_4 \cdot BF_3$ and 11.3% boron fluoride monohydrate; its properties were: $d_4^{20}$ 1.8784; $\kappa_{20} = 0.01029$; $\Omega^{-1}$ cm$^{-1}$; viscosity $\eta_{20}$ = 16.96 st. sec.; boron fluoride content 51%.

The benzene used in the reactions had the constants: m.p., + 5.0°; b.p. 79-80°; $d_4^{20}$ 0.8782, $n_D^{20}$ 1.5004; the 3-methylbutene-1 and the 2-methylbutene-2 were prepared by catalytic dehydration of isoamyl alcohol over granular aluminum oxide at 320-360°.

In the dehydration of the isoamyl alcohol over activated aluminum oxide, 3-methylbutene-1, 2-methylbutene-2, and 2-methylbutene-1 were formed; therefore, in order to prepare the pure olefins, the mixture of amylenes was treated at 0° with 75% sulfuric acid [4]; 3-methylbutene-1, which is insoluble in 75% sulfuric acid, remained in the upper layer which was separated from the lower, treated with a 20% solution of sodium hydroxide, washed with water to a neutral reaction of the wash water, dried over calcined calcium chloride, and distilled in a column having 20 theoretical plates. A fraction was collected at 19-20°, 753 mm Hg, which had the following constants: $d_4^{20}$ 0.6274; $n_D^{20}$ 1.3461; MR found 24.88, calculated for 3-methylbutene-1 24.90; literature data [5]: b.p. at 760 mm Hg 20.6°; $d_4^{20}$ 0.6272; $n_D^{20}$ 1.3643.

From the lower (acid) layer, after saponification, was taken a fraction boiling at 37-38°, 753 mm Hg, which was redistilled over metallic sodium in a column having 20 theoretical plates; the olefin prepared by this means had the following constants: b.p. 37-38° (753 mm Hg); $d_4^{20}$ 0.6595, $n_D^{20}$ 1.3863; MR found 24.93, calculated for 2-methylbutene-2 24.95; literature data [5]: b.p. 38.5° (760 mm Hg); $d_4^{20}$ 0.6620; $n_D^{20}$ 1.3869. A comparison of the experimental data with the literature data leads to the conclusion that the amylene with a b.p. of 19-20° (753 mm Hg) was 3-methylbutene-1, and that with a b.p. of 37-38° was 2-methylbutene-2.

The investigation of the alkylation of benzene with amylenes was carried out in a glass three-necked flask having a volume of 0.5 liter and fitted with a reflux condenser, a stirrer, and a capillary for the introduction of the olefin. The unreacted olefin was collected in a gasometer. The reaction mixture obtained after separation of the catalyst layer was treated in the usual manner.

The first experiments were carried out at a benzene-to-olefin ratio of 2:1, 2-methylbutene-2 as the olefin, a temperature of 50°, olefin addition time of 1.5 hours, and time of additional stirring of 1 hour. 78 g of benzene, 35 g of 2-methylbutene-2, and 11.7 g of catalyst were used in the reaction, and this yielded 48.6 g of a fraction boiling up to 180°, 40.4 g of a 180-210° fraction ($d_4^{20}$ 0.8746; $n_D^{20}$ 1.4949), and 24 g of a fraction boiling above 210° ($d_4^{20}$ 0.9463, $n_D^{20}$ 1.4890). The yield of alkylate (the fraction boiling above 180°) was 87.6% of theory.

**TABLE 1**

Total Content of Alkylbenzenes Obtained at a Mole Ratio of Benzene to 2-Methylbutene-2 of 2:1

| Reaction product | Composition in weight % | | $d_4^{20}$ | $n_D^{20}$ | Bromine number |
|---|---|---|---|---|---|
| | Alkylate | Polyalkylate | | | |
| Tert-amylbenzene | 63.0 | — | 0.8735 | 1.4951 | 0 |
| Di-tert-amylbenzene | 35.5 | 96.0 | 0.8500 | 1.4840 | 0 |
| Residue boiling above 290° | 1.5 | 4.0 | 0.8303 | 1.4601 | 18 |
| Total | 100.0 | 100.0 | — | — | — |

From the 180-210° fraction was separated, in 90% yield, a 189-191° fraction having $d_4^{20}$ 0.8735, $n_D^{20}$ 1.4951; from the fraction boiling above 210° was separated, in 93% yield, a fraction boiling at 258-260° having $d_4^{20}$ 0.8500; $n_D^{20}$ 1.4840. The inability of these aromatic hydrocarbons to undergo the nitration reaction of M. I. Konovalov [6] indicated the absence in the alkyl group of a hydrogen on the carbon atom directly connected with the phenyl group.

Nitration of the fractions indicated that mainly mono- and di-tert-amylbenzenes were formed by the alkylation of benzene with 2-methylbutene-2.

The intermediate fractions were mixtures of mono- and di-tert-amylbenzenes and also hydropolymers with the alkylbenzenes.

Under the conditions of the reactions, neither destruction nor isomerization of the 2-methylbutene-2 occurred, and, therefore, alkylation led mainly to the formation of only tert-amylbenzenes.

**TABLE 2**

Alkylation of Benzene with 3-Methylbutene-1 by Means of an Orthophosphoric Acid – Boron Fluoride Complex

| Experiment No. | Reaction temp., °C | Olefin addition rate, hours-4 (hour-1) | Mole ratio, $C_6H_6:C_5H_{10}$ | Catalyst, % | Yield of fractions in % of theory | | | Total content in alkylate of 189-191° fraction |
|---|---|---|---|---|---|---|---|---|
| | | | | | 180-210° | above 210° | 189-191° | |
| 1 | 50 | 1.5+1 | 2:1 | 10 | 52 | 35 | 46 | 60 |
| 2 | 50 | 1.5+1 | 2:1 | 15 | 55 | 33 | 49 | 63 |
| 3 | 50 | 1.5+1 | 2:1 | 20 | 59 | 31 | 52 | 65 |
| 4 | 50 | 1.5+1 | 2:1 | 25 | 61 | 30 | 54 | 67 |
| 5 | 50 | 4+1 | 2:1 | 15 | 59 | 31 | 51 | 66 |
| 6 | 50 | 2.5+1 | 2:1 | 15 | 58 | 31 | 51 | 65 |
| 7 | 50 | 0.5+1 | 2:1 | 15 | 53 | 34 | 47 | 61 |
| 8 | 0 | 1.5+1 | 2:1 | 15 | 35 | 47 | 30 | 42 |
| 9 | 15 | 1.5+1 | 2:1 | 15 | 43 | 41 | 37 | 50 |
| 10 | 30 | 1.5+1 | 2:1 | 15 | 48 | 37 | 42 | 58 |
| 11 | 80 | 1.5+1 | 2:1 | 15 | 65 | 25 | 57 | 71 |
| 12 | 50 | 1.5+1 | 1:1 | 15 | 33 | 46 | 29.2 | 42 |
| 13 | 50 | 1.5+1 | 2:1 | 15 | 55 | 37 | 49 | 63 |
| 14 | 50 | 1.5+1 | 3:1 | 15 | 57 | 32.6 | 50.2 | 64 |
| 15 | 50 | 1.5+1 | 4:1 | 15 | 59 | 30.2 | 51.7 | 66 |
| 16 | 50 | 1.5+1 | 8:1 | 15 | 65 | 27.0 | 57.0 | 70 |

Note: In the third column the first figure gives the time for addition of 35 g of olefin, and the second gives the stirring time for the reaction mixture after the addition of the olefin.

With the aim of defining more accurately the structures of the tert-amylbenzenes, the 189-191° fraction was subjected to hydrogenation. The products obtained were distilled, whereupon there was separated in 99% yield a fraction boiling at 198-199° with $d_4^{20}$ 0.8285 and $n_D^{20}$ 1.4547, which, according to literature data [5], corresponds to tert-amylcyclohexane having b.p. 193-195°, $d_4^{20}$ 0.8196, $n_D^{20}$ 1.4510.

For purposes of comparison, we synthesized tert-amylcyclohexane from p-tert-amylphenol by hydrogenation to p-tert-amylcyclohexanol which was dehydrated, and the resulting product was subjected to hydrogenation. The hydrogenation product was distilled in a column having 20 theoretical plates; the main mass of the hydrocarbons distilled at 198-199° and had $d_4^{20}$ 0.8289, $n_D^{20}$ 1.4547.

With complete assurance, it can be asserted that the 189-191° fraction of the hydrogenation product, and also the product synthesized through p-tert-amylphenol were tert-amylcyclohexane. Consequently, the 189-191° fraction was tert-amylbenzene (2-phenyl-2-methylbutane).

The alkylation of benzene with 3-methylbutene-1 by means of 88.7% $H_3PO_4 \cdot BF_3$ : 4 11.3% $H_2O \cdot BF_3$ also leads to the formation of tert-amylbenzenes. Preparations of such alkylbenzenes is possible owing to isomerization of the original 3-methylbutene-1 into 2-methylbutene-2, which apparently occurs in the alkylation process.

The isomerization of 2-phenyl-3-methylbutane, the expected product, into 2-phenyl-2-methylbutane does not take place. There was available to us 2-phenyl-3-methylbutane having $d_4^{20}$ 0.8790, $n_D^{20}$ 1.4882, and 50 g of this material together with the $H_3PO_4 \cdot BF_3$ catalyst (23.4 g) was charged to a 0.25-liter three-necked flask, and the mixture was vigorously stirred for 5 hours at 50°. The reaction mixture was then washed with water, a 20% solution of sodium hydroxide, and again with water to a neutral reaction of the wash water, after which it was distilled over sodium; the main mass of the product boiled at 185-186° and had $d_4^{20}$ 0.8792, and $n_D^{20}$ 1.4881. The density and the refractive index of the original hydrocarbon and those of the alkylbenzene obtained after the treatment of the 2-phenyl-3-methylbutane with $H_3PO_4 \cdot BF_3$ catalyst agreed closely; oxidation gave benzoic acid, and nitration by the method of M. I. Konovalov [6] gave a tertiary nitro compound. Consequently, the alkylbenzene obtained was the original, unchanged 2-phenyl-3-methylbutane.

**TABLE 3**

Total Content of Alkylbenzenes Obtained at a Mole Ratio of Benzene: 3-methylbutene-1 of 1:1

| Reaction products | Composition in weight % | | $d_4^{20}$ | $n_D^{20}$ | Bromine number |
|---|---|---|---|---|---|
| | Alkylate | Polyalkylate | | | |
| Tert-amylbenzene | 42.0 | — | 0.8784 | 1.4951 | 0 |
| Di-tert-amylbenzene | 55.4 | 95.5 | 0.8500 | 1.4840 | 0 |
| Residue boiling above 250° | 2.6 | 4.5 | 0.8265 | 1.4569 | 21 |
| Total | 100.0 | — | — | — | — |

The conditions investigated for the alkylation of benzene with 3-methylbutene-1 had no effect on the type of alkylbenzenes formed; the formation of only tert-amylbenzenes was detected in all cases.

In the experiments, 35 g of amylenes was used, the amount of benzene varied depending on the mole ratio, and the amount of catalyst varied from 7.8 to 19.5 g. The effect of temperature on the alkylation of benzene with amylenes was investigated in the range 0 to 80°. An increase in temperature caused an increase in the yield of mono-tert-amylbenzene and a decrease in the yield of di-tert-amylbenzene. Thus, if the yields at 0° of tert-amylbenzene and di-tert-amylbenzene were, respectively, 42 and 47%, then at 80° the yields became 71 and 25%. The results of the investigation are presented in Table 2.

The composition of the alkylate, as in alkylation with propylene, isobutylene, and n-butene, depends chiefly on the mole ratio benzene: olefin. If at a ratio of benzene to 3-methylbutene-1 of 1:1 the alkylate contains 42% tert-amylbenzene, then at a ratio of 2:1 its content becomes 63%; further increase in the ratio benzene: olefin insignificantly increases the content of tert-amylbenzene, which becomes 70% at 8:1.

At benzene: amylene ratios greater than 2:1, the alkylate practically consists of tert-amylbenzene and di-tert-amylbenzene. The content of di-tert-amylbenzene increases from 30 to 55.4% at ratios of 8:1 and 1:1, respectively, and is greater than the polyalkylbenzene content in alkylation with propylene, n-butene, and isobutylene. Here, to a greater degree, in the yield and composition of the mono-alkylbenzenes and polyalkylbenzenes is indicated the effect of the size and structure of the alkyl group.

The alkylates obtained at high amylene addition rates and low benzene: amylene ratios contained products of the polymerization and hydrodehydropolymerization of 2-methylbutene-2 and 3-methylbutene-1.

The alkylation of benzene with amylenes shows that in this reaction the complex of orthophosphoric acid and boron fluoride possesses high alkylating activity.

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Received November 14, 1955

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* T. p. = C. B. Translation pagination.